SOL-GEL METHODOLOGIES FOR THE PREPARATION OF NEW COMPOSITE CATION-EXCHANGERS AND THEIR ANALYTICAL AND ELECTROANALYTICAL APPLICATIONS

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

APPLIED CHEMISTRY

BY

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2010

Dedicated

to

My Parents

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This is to certify that the thesis entitled "*Sol-gel methodologies for the preparation of new composite cation-exchangers and their analytical and electroanalytical applications*" and being submitted by *Mrs. Tabassum Akhtar* for the award of the degree of *Doctor of Philosophy* in Applied Chemistry faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, India. Is entirely is based on the experimental work created out by her under my supervision. The work reported in this thesis embodies the work of the candidate himself and is original one has not been submitted to any one University or Institution for the award of any degree of diploma.

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ACKNOWLEDGEMENTS

I am most indebted to the grace of the Almighty "One Universal Being", who inspires entire Humanity to knowledge, and to give me required favor to complete this work.

I would like to express my deep sense of gratitude to my supervisor Prof. Asif Ali Khan, for his invaluable guidance and constant encouragement throughout this work. His subtle ways of encouragement helped me, as a beginner in journey in to the depth of my research work. His cooperation, wise advice, suggestion and guidance through the months have brought me to the point of successfully completing this thesis work. His systematic and analytical approach blended with constructive criticism and innovative ideas helped me to understand the basics of research and to overcome many experimental hurdles. I am grateful to him for teaching me discipline and hard work. His straightforward approach and healthy criticism have always proved to be rewarding. I especially appreciate the freedom he has provided me during my course of Ph.D Work.

Indeed, it is my profound privilege to acknowledge gratitude to Prof. Ali Mohammad, Chairman, Department of Applied Chemistry, Z.H. College of Engineering and Technology, Aligarh Muslim University, Aligarh for his constant encouragement throughout the course of investigation.

I wish to thank my senior colleague Dr. Inamuddin for his valuable suggestions, guidance, and constant inspiration and help when I needed. Much is owed to my senior colleague Dr Anis Khan beyond words can express.

I am also thankful to my junior colleagues and also my friends Leena Paquiza, Umme Habiba and Shakeeba Shaheen for generous support.

Special thanks are also due to non-teaching staffs of this Department for their cordial cooperation.

It ventilates my profound sense of obligations to my friends, especially Sadaf Khan and Saema Usmani, for their timely help, good wishes, encouragement and affections.

Assistance provided by the A.I.I.M.S. Delhi, I.I.T. Roorkee and I.I.T. Delhi to carry out some instrumental analyses and financial assistance provided by A.M.U. are also thankfully acknowledged.

I am also in debt of love, affections, encouragement provided in the path of the research work by my younger and elder sisters, brothers, brother-in-law, bhabi and all my in-laws especially late mother-in-law and Arshiya baji.

Last but not least, I feel short of words and full of emotions in thanking my parents for the unconditional love, constant inspiration and support they have provided.

I have no words to express my heartiest thanks and gratitude to my dear husband Mr. Hirasat Ali Siddiqi whose affection, encouragement, sacrifices, support and blessing have always been the most vital source of inspiration to me. I am highly thankful to God who has gifted me with cooperative and supportive relatives.

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ABSTRACT

"Sol-gel methodologies for the preparation of new composite cation-exchangers and their analytical and electroanalytical applications".

There has been substantial research on the inorganic ion-exchangers as well as organic resins commonly known as ion-exchange media for the remediation of wastewater containing heavy metal ions as a by product of various industries. However the practical use of organic and inorganic ion-exchange media are still limited. Further more inorganic ion-exchangers cannot be used in convenient way in case when the impurities from a large volume of effluent are to be removed. In this connection, research has motivated to the investigators to study of organic-inorganic composite ion-exchangers with better mechanical, chemical, thermal and radiation stabilities, reproducibility and possessing good selectivity for heavy toxic metals, indicating its useful environmental applications. As early as the late 1980s, molecular level combination between organic polymers and inorganic materials has been of interest. The resulting materials i.e., the organic–inorganic composite materials have also attracted a great attention since then in the field of material science because of their unique opportunity to combine the remarkable features of organic compounds with those of inorganic materials. Among a wide variety of applications of hybrid materials explored, the ones that possess ion-exchange properties have recently drawn particular interest since ion-exchange is important for a variety of applications such as water treatment, chemical separation, and electrochemical sensing. With these considerations, in our present work three organic–inorganic composite cation-exchange materials based on poly-o-toluidine and Nylon-6,6 have been chemically prepared by the sol-gel mixing of organic polymer with the inorganic ion-exchanger precipitates of multivalent metal acid salts, i.e., Zr(IV) phosphate, Ce(IV) phosphate and Sn(IV) phosphate, respectively.

Finding of the Work Done

The research work done in the thesis entitled *"Sol-gel methodologies for the preparation of new composite cation-exchangers and their analytical and electroanalytical applications"* is compiled in eight chapters:

Chapter – 1 entitled *"General Introduction"* gives a detailed definition and classification of composite materials and nano-composite materials. A brief history, preparation and properties of polymer matrix composite i.e. organic-organic and organic-inorganic composites, have been discussed. Special interests are focused on electrically conducting composite materials. Historical background of chromatography. Critical reviews of the studies on inorganic ion-exchangers, organic resins, intercalating ion-exchangers, chelating ion-exchangers and '*organic-inorganic*' composite materials used as synthetic ion-exchangers, electrically semiconductors, ion-exchanger membranes, ion-selective electrodes, etc. have also been given based on the literature survey which reveal the some of the novel applications of these materials.

Chapter – 2 entitled *"Preparation and characterization of Poly-o-toluidine Zr(IV) phosphate, Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate cation-exchange materials"*, the main points of this chapter are the preparation and characterization of three organic-inorganic cation-exchangers i.e. poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate. The physico-chemical properties of these composite materials (S-5, T-4 and P-4) were determined using some instrumental techniques, such as SEM, FTIR, and simultaneous TGA/DTA, powder XRD, UV-VIS spectrophotometry, AAS, elemental analyses etc. The composite materials (poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate) were found in nano-particles range while Nylon-6,6 Sn(IV) phosphate is fibrous cation-exchanger having high thermal and chemical stabilities.

Chapter – 3 entitled *"Ion-exchange properties of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate & Nylon-6,6 Sn(IV) phosphate composite cation-exchanger materials"*, in this chapter ion-exchange properties of the materials were carried out such as ion-exchange capacity, effect of eluent concentration on the ion-exchange capacity, the

lution behavior, pH-titration, thermal effect on ion-exchange capacity, distribution tudies for metal ions and ion-exchange kinetics of various metal ions. On the basis of istribution studies poly-o-toluidine Zr(IV) phosphate sample (S-5), and Nylon-6,6 n(IV) phosphate sample (P-4) cation-exchangers were found to be highly selective wards Hg(II) while poly-o-toluidine Ce(IV) phosphate sample (T-4) was found to be ighly selective towards Cd(II), which are the major polluting elements in the water. The n-exchange kinetic studies carried out on composite cation-exchangers indicated that ie ion-exchange process taking place on the surface of the materials is a particle iffusion controlled phenomenon and it also revealed that equilibrium is attained faster at higher temperature. Some physical parameters like self diffusion coefficient (D_0), nergy of activation (E_a) and entropy of activation (ΔS^o) have been evaluated under onditions favoring a particle diffusion-controlled mechanism.

hapter – 4 entitled *"Electrical conductivity measurement studies on poly-o-toluidine Zr(IV) hosphate & poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchange materials"* eals with the electrical conducting behavior of poly-o-toluidine Zr(IV) phosphate & oly-o-toluidine Ce(IV) phosphate composite cation-exchange materials while Nylon-6,6 n(IV) phosphate is non-conducting cation-exchange material. Various samples of the omposites were prepared using the method described in Chapter – 2 by mixing of poly--toluidine organic monomers into inorganic precipitates of Zr(IV) phosphate and Ce(IV) hosphate, respectively. Among these, sample S-5 sample T-4 were selected for detail lectrical conductivity studies, with increasing temperature (between 30 °C to 200 °C) ere carried out. On examination, it was observed that the electrical conductivity of the omposite samples increase with the increase in temperature upto 120 °C thereafter ecreases and the values lie in the order of 10^{-2} to 10^{-3} S/cm^{-1} for poly-o-toluidine Zr(IV) hosphate and poly-o-toluidine Ce(IV) phosphate i.e.; in the semiconductor region. sothermal electrical conductivity measurement studies were carried out from 30 to 200 C at an interval of 15 minutes. These composites were also observed to be stable naterials, *i.e.* the room temperature conductivities are negligibly affected by short-term xposure to laboratory.

Chapter – 5 entitled *"Preparation and Characterization of composite cation-exchanger membrane and their applications in making Ion-Selective membrane electrode Using: Poly-o-toluidine Zr(IV) phosphate, Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate"* deals the preparation and characterization of the ion-exchanger membranes and ion-selective membrane electrodes using the composite cation-exchange materials as an electroactive components.

Composite cation exchangers poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate were used as electroactive material embedded in inert polymer binder (PVC or Araldite), for the preparation of heterogeneous ion-selective membrane electrodes. The physico-chemical properties of the membranes *viz.*, thickness, water content, porosity, swelling etc. were also determined. Since the composite cation-exchangers poly-o-toluidine Zr(IV) phosphate (S-5), and Nylon-6,6 Sn(IV) phosphate (P-4) having selectivity towards Hg(II) while poly-o-toluidine Ce(IV) phosphate (T-4) shown selectivity towards Cd(II), respectively; the membranes were equilibrated with the solutions of selected ions of Hg(II) and Cd(II), and then taken for potentiometric studies.

Chapter – 6 entitled *"Analytical and Electroanalytical Applications of Poly-o-toluidine Zr(IV) phosphate, Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate cation-exchangers"* deals with the various analytical and environmental applications of the proposed composite materials to achieve quantitative binary separations of some important metal ions of analytical utility on poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate columns. The practical utility of the proposed membrane sensors assembly was also tested by its use as an indicator electrode in the potentiometric titration of Hg(II) and Cd(II) with EDTA.

Chapter –7 entitled *"Adsorption and Electroanalytical studies on nano- composite poly-o-toluidine Zr(IV) phosphate for Ziram (Zinc(II) dimethyldithiocarbamate)"* deals with the study poly-o-toluidine Zr(IV) phosphate, a nano-composite cation-exchanger is used for the adsorption studies of Ziram and some important thermodynamic parameters were also

determined. Such adsorption studies of pesticides on composite materials can help us in making pesticide sensitive membrane electrode that can be used to determine pesticide in trace amounts in the given sample of polluted water. However the main objective of the present work is to developed electroanalytical method by making Ziram [zinc(II) bis(dimethyldithiocarbamate)]sensitive membrane electrode to determine Ziram in traces amounts in water.

Chapter – 8 entitled *"Adsorption thermodynamics studies of 2,4,5-trichlorophenoxy acetic acid on poly-o-toluidine Zr(IV) phosphate, a nano-composite cation exchanger:as pesticide sensitive membrane electrode"* deals with study poly-o-toluidine Zr(IV) phosphate, a nano-composite cation exchanger is used for the adsorption studies of 2,4,5-T and some important thermodynamic parameters were also determined. On the basis of adsorption studies, a pesticide sensitive electrode was fabricated by using poly-o-toluidine Zr(IV) phosphate composite material. The purpose of this work was to evaluate the adsorption potential of poly-o-toluidine Zr(IV) phosphate cation-exchanger for 2,4,5-trichlorophenoxy acetic acid. The equilibrium data of the adsorption process were then studied to understand the adsorption mechanism of 2,4,5-T molecules onto the prepared cation-exchanger.

In conclusion, we can say that in comparison compared with other ion-exchange materials of this class 'organic-inorganic' composite materials offer more advantages. A number of analytical applications of these materials such as separation of metal ions, determination of toxic heavy metals from waste water, in making ion-selective membrane electrodes and semi-conducting properties would make these materials important for materials as well as environmental scientists.

Suggestions for Future Work

The research work done in this thesis may be continued for the development of the materials of desirable properties by the new researchers of this discipline in the following directions-

- To develop simple, selective and economical "organic-inorganic" composite ion-

exchange materials having selectivity towards heavy toxic metal ions and especially for radioactive elements coming from a high temperature radioactive waste streams to decrease the pollution load of the environment.

- To develop fibrous type composite ion-exchangers of recent origin having capability for obtaining in different forms such as conveyer belts, non-woven materials, staples, nets and cloths *etc.* These open new and novel possibilities, of using these materials in various industrial applications and in environmental analysis.
- To study the adsorption of pesticides on the composite cation-exchanger to reduce water and soil pollution load.
- To develop electrically conducting nano-composite materials with higher electrical conductivity for their use in various electronic and photonic systems.
- To more studies of electrical behavior of electrically conducting "organic-inorganic" composite ion-exchange materials.
- To study about the ion-exchange kinetics and adsorption of pesticides (adsorption thermodynamics) on these materials.
- The DC electrical conductivity of the composites may also be utilized as electrochemical sensor to evaluate toxic gases, volatile organic compounds and humidity sensing characteristics of these composites.
- Furthermore, to study in detail, the electrically conducting composite ion-exchange materials used as electrochemically switchable ion-exchangers for water treatment; especially for water softening.
- Efforts will be made to use these composites as adsorbents for air (*i.e.* gas separations) by controlling their electrical conductivity.
- A detailed study of composite ion-exchangers used as catalysts for reaction of gases and of liquids or solutes.
- Chromatographic and thin layer separation, identification and determination of pharmaceuticals and related drugs in drugs formulations and biological samples.
- To develop ion-selective electrodes for a number of heavy toxic elements with detection limits down to parts-per-million levels 10^{-10} M, which is possible by studying the underlying chemical principles and modifying the nature of electroactive materials.

Chapter-1

General Introduction and Literature Review

Methods of Chemical analysis is one of the most important branch of chemical sciences applicable to industry and environmental sciences. Different chromatographic techniques are used in the separation of complexed mixture for identification and determination of components present in the mixture. While most other types of chromatography are used principally for separation of complex organic substances, ion-exchange chromatography is particular of well suited for the separation of inorganic ions, both cations and anions, because the separation is based on exchange of ions in the stationary phase. Ion-exchange material (stationary phase) plays an important role in separation of different charged components. These ion-exchange materials can be classified in the following ways:

1. Inorganic Ion-exchange materials
2. Organic-exchange materials
3. Organic-inorganic composite ion-exchange materials

1.1 Ion-Exchange Materials: An Introduction and Literature Review

1.1.1 Inorganic ion-exchange materials

Creating chemical compounds with the desired physical and chemical properties produces synthetic ion-exchangers. On the basis of chemical characteristics, synthetic inorganic ion-exchangers are classified as follows:

- Synthetic zeolites (aluminosilicates)
- Hydrous oxides of metals
- Acidic salts of polyvalent metals
- Insoluble salts of heteropolyacids
- Insoluble hydrated metal hexacyanoferrate (II) and (III) (Ferro cyanides)

Other substances with weak exchange properties

Zeolites were the first inorganic materials to be used for the large-scale removal of waste effluents. Zeolites are crystalline alumino-silicate based materials and can be prepared as microcrystalline powders, pellets or beads. The main advantages of synthetic zeolites when compared with naturally occurring zeolites are that they can be engineered with a wide variety of chemical properties and pore sizes, and that they are stable at higher temperatures.

The main limitations of synthetic zeolites :

- They have a relatively high cost compared with natural zeolites;

- They have a limited chemical stability at extreme pH ranges (either high or low);
- Their ion specificity is susceptible to interference from similar sized ions;
- The materials tend to be brittle, which limits their mechanical stability;

1.1.2 Organic ion-exchange materials

The largest groups of ion-exchangers available today are synthetic organic resins in a powdered (5–150 μm) or bead (0.5–2 mm diameter) form. The framework, or matrix, of the resins is a flexible random network of hydrocarbon chains. This matrix carries the ionic groups such as: $-SO_3^-$, $-COO^-$, $-PO_3^{2-}$, $-AsO_3^{2-}$ *etc.* in cation-exchangers, and $-NH_3^+$, $-NH_2^+$, $-N^+$, $-S^+$ etc. *in anion-exchangers. Ion-exchange resins thus are cross-linked* polyelectrolytes. The resins are made insoluble by cross-linking the various hydrocarbon chains. The degree of cross-linking determines the mesh width of the matrix, swelling ability, movement of mobile ions, hardness and mechanical durability. Highly cross-linked resins are harder, more resistant to mechanical degradation, less porous and swell less in solvents. When an organic-ion exchanger is placed in a solvent or solution it will expand or swell. The degree of swelling depends both on the characteristics of the solution/solvent and the exchanger itself and is influenced by a number of conditions, such as:

- The solvent's polarity,
- The degree of cross-linking,
- The exchange capacity,
- A strong or weak salvation tendency of the fixed ion groups,
- The size and extent of the salvation of counter ions,
- The concentration of the external solution,
- The extent of the ionic dissociation of functional groups.

The main advantages of synthetic organic ion-exchange resins are their high capacity, wide applicability, wide versatility and low cost relative to some synthetic inorganic media. The main limitations are their limited radiation and thermal stabilities. At a total absorbed radiation dose of 10^9 to 10^{10} rads most organic resins will exhibit a severe reduction in their ion exchange capacity (10 to 100% capacity loss), owing to physical degradation at both the molecular and macroscopic leval.

1.1.3 Chelating ion-exchange materials

The use of ligand or complexing agent in solution in order to enhance the efficiency of separation of cation mixtures (*e.g.* lanthanide) using conventional cation or anion-exchange resins is well established. An alternative mode of application of complex formation is, however, the use of chelating resins that are ion-exchangers in which various chelating groups (*e.g.* dimethylglyoxime, iminoacetic acid *etc.*) have been incorporated and are attached to the resin matrix. These types of chelating ion-exchangers have been developed recently and their analytical applications explored [1]. Complexions have been used for the preparation of new chelating resins for separating metal ions on the basis of complex formation [2]. A number of such ion-exchangers have been prepared by the incorporation of ligands on resins [3]. 8-hydroxy quinoline [4] sobbed on porasil is capable of separating metal ions at trace level. Ferrochrome black–T modified graphite columns have been used for the separation of metal ions [5]. A PAN [1-(2-pyridylazo-2-napthol)] sobbed zinc silicate [6] has been used for the recovery of precious metal ions Pt^{4+} and Au^{3+}, and ammonium-molybdophosphate [7], has been used for the quantitative separation of Cs^{+} ions. Separation and retention behavior of metal ions have been achieved on tetracycline hydrochloride coated alumina [8] and zirconium(IV) selenomolybdate [9], while tetracycline hydrochloride sobbed zirconium(IV) tungstophosphate chelating exchanger has been employed in the separation of La^{3+} ions [10]. An important feature of chelating ion-exchangers is the greater selectivity, which they offer compared with the conventional type of ion-exchanger. The affinity of a particular metal ion for a certain chelating resin depends mainly on the nature of the chelating group. And the selectivity behavior of the resin is largely based on the different stabilities of the metal complexes formed on the resin under the various pH conditions.

1.1.4 Intercalation ion-exchangers

After the development of various types of inorganic ion-exchange materials, lately much interest has been developed in the study of pillared inorganic materials and intercalation compounds (new porous intercalates) that can be synthesized by introducing some organic molecules in the matrix of layered inorganic ion-exchangers. The main advantage of a pillared structure is that it allows ready access of large ions and complexes to the interior due to the increase in the inter layer distances and pore sizes. This is very useful in radioactive waste cleanup. Amongst the new developments of ion-exchangers,

intercalation compounds have played an important role in the field of separation science and technology. These compounds can be synthesized by introducing some organic ions or molecules in the matrix of inorganic ion-exchangers. Alumina, kaolin, clays, bentonite, pectin, alginic acid *etc.* have been used as adsorbent with stimulated considerable interest in medical science throughout world. Hence, intercalation is a process in which neutral polar molecules are inserted between the sheets of a layered insoluble compound.

Alberti et al. [11] have reported the synthesis and characterization of a new type of zirconium phosphate by the name of zirconium phosphate hemihydrate [α-Zr $(HPO_4)_{0.5}$. H_2O]. A large number of other new materials have also been prepared on zirconium phosphate by pillaring methods. *Alberti* and *coworkers* [12] have intercalated α-Zr(IV)$(RPO_3)_2.H_2O$ by phenyl containing $-SO_3H$ groups and γ - Zr(IV)$(PO_4)(H_2PO_4).2H_2O$ by crown ether. *U. Costantino* [13] has given a detailed description of intercalation of alkanols and glycols into α -Zr(HPO_4). H_2O and also developed zirconium phosphate-phosphite [14]. *Clearfield* and *Tindwa* [15] have studied in detail the uptake of n-phenyl amine, n-butyl amine and ethylene diamine on α–$Zr(HPO_4)_2.H_2O$. *Dines et al.* [16] have prepared monophenyl; diphenyl and triphenyl bridging pillared zirconium phosphates by using phenyl disulphonic acids to bridge across the layers. They have also shown that it is possible to form three – dimensional or pillared analogous of the phosphonates by utilizing α, ω - diphosphonic acids. *Varshney et al., Rawat et al., Singh et al.* and *Qureshi et al.* have also studied on amine tin(II) hexacyanoferrate(II) [17], tin(IV) diethanol amine [18], iron(III) diethanol amine [19] and zirconium(IV) ethylene diamine [20] respectively.

Recently, some intercalation ion-exchangers have been developed and reported in the literature. *Hudson et al.* [21] have reported the intercalation of monoamine into α-$Sn(HPO_4)_2.H_2O$ and investigated the ion-exchange behavior of amine in the presence of transition metal ions. *Wang et al.* have reported the selective separation of Cs^+ on zirconium phenyl diphosphonate phosphate [22]. *Chudasama et al.* [23] synthesized a new inorganic-organic ion-exchanger by anchoring p-chlorophenol to $Zn(WO_4)_2$ and reported the material has a good ion- exchange capacity and stability. *Malik et al.* [24] have reported pyridinium tungstoarsenate, selective for Rb^+ and Cs^+ and *Singh et al.* intercalated aniline into tin(IV) phosphate [25] and Zr(IV)phosphate, $[(ZrO_2)_2.(C_6H_5NH_2)HPO_3. 3.7H_2O]$; selective for Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} [26]. *Nabi et al.* have reported the synthesis, characterization and analytical applications of Zr(IV)

sulfosalicylate [27] (selective for Ag^{+} and Hg^{2+}) and pyridinium-tin(IV) tungstoselenate [28].

1.2 Composite Materials

Composite materials are classical engineering materials made from two or more constituent materials that remain separate and distinct on a macroscopic level while forming a single component with identifiable interfaces [29-46]. The properties of the new material are dependent upon the properties of the constituent materials as well as the properties of the interfaces.

1.2.1 Composite theory

A combination of two or more materials (reinforcing elements, fillers, and composite matrix binder), differ in form or composition on a macroscale. The constituents retain their identities, that is, they do not dissolve or merge completely into one another although they act in concert. Normally, the components can be physically identified and exhibit an interface between one another. Examples are cermets and metal-matrix composites.

Society has always wanted and continued to seek materials that are strong, tough, and light. In this quest, it was discovered that the macroscopic combinations of two or more different materials resulting in a new material with improved properties could be described as "composite" [47]. Naturally occurring composites are bone, bamboo, feathers, natural fibers, and wood. Bone is an organic-inorganic composite of protein (collagen) and minerals (calcium apatite) and bamboo is cellulose reinforced by silica. These combinations make a hard material with high impact strength. The cellulose cell structure of wood and fiber is bound together with lignin, a natural polymeric substance.

1.2.2 Classification of composites

Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different form those of any of the constituents.

Matrix phase the primary phase, having a continuous character, is called matrix. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it.

Dispersed (reinforcing) phase the second phase (or phases) is imbedded in the matrix in a discontinuous form. This secondary phase is called dispersed phase. Dispersed phase is usually stronger than the matrix, therefore it is sometimes called reinforcing phase. Many of common materials (metal alloys, doped Ceramics and Polymers mixed with additives) also have a small amount of dispersed phases in their structures, however they are not considered as composite materials since their properties are similar to those of their base constituents (physical properties of steel are similar to those of pure iron).

There are two classification systems of composite materials. One of them is based on the matrix material (metal, ceramic, polymer) and the second is based on the material structure:

I. Classification of Composites based on Matrix Material

1. Metal Matrix Composites (MMC)

Metal Matrix Composites are composed of a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and a dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase.

2. Ceramic Matrix Composites (CMC)

Ceramic Matrix Composites are composed of a ceramic matrix and imbedded fibers of other ceramic material (dispersed phase).

3. Polymer Matrix Composites (PMC)

Polymer Matrix Composites are composed of a matrix from thermoset (Unsaturated Polyester (UP), Epoxiy (EP)) or thermoplastic (Polycarbonate (PC), Polyvinylchloride, Nylon, Polysterene) and embedded glass, carbon, steel or Kevlar fibers (dispersed phase).

II. Classification of Composite Materials based on Reinforcing Material Structure

1. Particulate composites

Particulate composites consist of a matrix reinforced by a dispersed phase in form of particles.

(i) Composites with random orientation of particles.

(ii) Composites with preferred orientation of particles. Dispersed phase of these materials consists of two-dimensional flat platelets (flakes), laid parallel to each other.

2. Fibrous composites

(i) Short-fiber reinforced composites: Short-fiber reinforced composites consist of a matrix reinforced by a dispersed phase in form of discontinuous fibers (length < 100*diameter).

(a) Composites with random orientation of fibers.

(b) Composites with preferred orientation of fibers.

(ii) Long-fiber reinforced composites: Long-fiber reinforced composites consist of a matrix reinforced by a dispersed phase in form of continuous fibers.

(a) Unidirectional orientation of fibers.

(b) Bidirectional orientation of fibers (woven).

3. Laminate composites

When a fiber reinforced composite consists of several layers with different fiber orientations, it is called multilayer (angle-ply) composite.

1.2.3 Nanocomposite materials

Conventional, macroscopic composite materials such as adobe is a mixture of clay and straw that serves as an effective structural composite material which has been used to make bricks and wall in arid regions and these along with reinforced concrete has shaped our world during the past. Yet when it comes to the microscopic world, reduced particle size boosts the importance of the interphase in composite mixtures and this is especially important for a new class of recently developed materials named, the nano-composites. The definition of "nanocomposite material" has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional materials, amorphous or crystalline, made of distinctly dissimilar components which are mixed at the nanometer scale.

Nanocomposite is a distinct form of composite materials, which involves embedding nano or molecular domain sized particles into an organic poly mer, metal or ceramic matrix material [48-54]. In all cases, it is perceived that the intimate inclusion of these nanoparticles in these matrices can completely change the properties of these materials. The nanoparticles can serve as matrix reinforcement in

order to change the physical properties of these base materials. With such small inclusions, a large amount of interfacial phase material is now included in the bulk of these nanocomposites, enabling a complete transformation of the material's chemical, mechanical and morphological domain structure. Much of today's research activity in the field of polymer based organic-inorganic hybrid nanocomposites exhibits mechanical, electrical properties superior to those of their separate components.

Nanocomposite plastics have their origin in the 1970's with the use of sol-gel technology to form homogeneous dispersions of small sized inorganic particles throughout a polymer matrix. In such systems, the inorganic phase may or may not be chemically attached to the organic phase. These first generation nanocomposites have been found to be useful in coating applications. Subsequently during 1980's, second generation nanocomposites emerged as a result of the resurgence in the use of fine particles, minerals and clay fillers for plastics. Limited compatibility between the filler and polymers as well as complex polymer processing requirements was needed to form these nanocomposites. In the 1990's and beyond, a new form of nanocomposite has emerged third generation nanocomposites where polymeric materials are reinforced with nanofibers such as carbon nanotubes, SiC whiskers, colloidal silica, nano-clay particles etc. This unique ability to obtain control of the nanoscale structures via innovative "bottom-up" synthetic approaches has consequently entailed several challenges and opportunities. Undertaking this challenge provides an opportunity for developing new materials with synergic behavior leading to improved performance [55].

1.3. Ion-Exchange Properties of Materials

1.3.1 Ion-exchange phenomenon & its historical background

The phenomenon of ion exchange is not of a recent origin. Many million years ago it had occurred in various sections of the globe. For example, some ions like potassium and lithium of patalite of pegmatite veins had been replaced with rubidium and cesium ions of step wisely fluid from the mega. This is nothing but ion-exchange phenomenon between minerals like patalite (solid phase) and fused salt fluid (liquid phase). It is well known that ion exchange has been playing very important roles during the course of weathering; aqueous rocks, clay rocks and soils being very effective ion-exchangers. Since life had been created in the sea, ion-exchange through bio-membranes between living organs and outside matters has been giving the essential motive forces to life and its evolution. The

earliest of the references were found in the Holy Bible establishing Moses' priority that succeeded in preparing drinking water from brackish water [56], by an ion-exchange method. Later on, Aristotle found the seawater loses part of its salt contents when percolated through certain sand [57]. In Egypt and Greece as well as in China, ancient people were clever enough to use some soils, sands, natural zeolites and plants as the tools for improving the quality of drinking water by way of desalting or softening. However, they were not aware of the actual phenomenon occurring in the process. Basically, ion exchange is a process of nature occurring throughout the ages before the dawn of civilization, has been embraced by analytical chemists to make use of difficult separation easier and possible.

Francis Bacon in 1623 brought the intentional use of ion exchange, without knowledge of its theoretical nature, based purely on empirical experiences and he described a method for removing salts from seawater. The first half of the 19th century was characterized by the appearance of the first information leading to the discovery of the ion-exchange principle, based primarily on the work of soil chemists. *Thompson, Spence* and *Way* in 1850 described independently that calcium and magnesium ions of certain types of soils could be exchanged for potassium and ammonium ions [58,59]. They defined the special properties of soil as *'base exchange'*. In the second half of the 19th century, agro chemists published a great number of papers dealing with ion exchange in soils. *Eichhorn* (in 1858) demonstrated exchange processes are reversible in soils [60]. In 1859, *Boedecker* proposed an empirical equation describing the establishment of equilibrium on inorganic ion-exchange sorbents. In the 20th century, the majority chemists believed that the *'base exchange'* in soils is nothing but a sort of absorption. Strong supports to ion-exchange come out with the synthesis of materials from clay, sand and sodium carbonate by *Gans* [61].

The discovery and development of the theory of ion exchange was reflected in practical applications. *Gans* developed the basis for the synthesis and technical application of inorganic cation-exchangers at the beginning of the 20th century. He termed the amorphous cation-exchangers based on aluminosilicate gels "permutated", having broad application, were actually the first commercially available ion-exchangers. In 1917, *Folin* and *Bell* developed an analytical method based on these materials for the separation and collection of ammonia in urine [62]. However, the usefulness of these synthetic zeolites was limited because of their low chemical and mechanical stability, ion-exchange

capacity that led the chemists to seek alternatives. During the period between the 1930s and 1940s, inorganic ion-exchange sorbents were replaced in almost all fields by the new organic ion-exchangers. The observation of *Adam* and *Holms* [63] that the crushed phonograph records exhibit ion-exchange properties, eventually resulted in the more significant development of synthetic ion-exchange resins (high molecular weight organic polymers containing a large number of ionic functional groups) in 1935. No scientist could then neglect ion-exchange phenomenon. However, it took nearly 85 years for the ion-exchange phenomenon to be fully recognized in chemistry since its scientific finding and understanding by *Thompson* and *Way*.

Just as applications of the organic resins are limited by breakdown in aqueous systems at high temperatures and in presence of high ionizing radiation doses; for these reasons there had been a resurgence of interest in inorganic exchangers in the 1950s. One of the possible ways of solving these problems involved replacing the organic skeleton of the ion-exchanger by an inorganic skeleton. Pioneering work was carried out in this field by the research team at the Oak Ridge National University led by *Kraus*, and by the English team led by *Amphlett*.

Further extensive research and study of inorganic ion-exchange sorbents were carried out in the 1960s and 1980s. Research led from the original amorphous type of ion-exchange sorbents to the study of crystalline ion-exchange materials. Clearfield and co-workers made great contributions in this area. Since last two decades, intense research has continued on the synthesis of a number of new 'organic-inorganic' composite materials having excellent properties that not only met the requirements of modern laboratories but also led to solution of previously insolvable problems. An interest of inorganic as well as composite ion-exchange materials in ion-exchange operations in industries is increasing day by day as their field of applications is expanding.

1.3.2 Ion-exchange chromatography

Ion-exchange chromatography a powerful tool for chemical separations was the first of the various liquid chromatography (L.C) methods to be used under modern L.C conditions. The wide scope of this technique is the product of the labors of many people. It has grown in response to practical needs. Most environmental samples have complex composition, thus separation and preconcentration of analyses are essential for accurately as well as precisely trace determination of elements in environmental samples. Ion-

exchange chromatography is an excellent technique that permits selective separation by the appropriate combination of ion-exchanger and eluent. Columns of ion-exchange materials [64-71] have been extensively used for the separation of amino acids, inorganic ions (especially rare earths), multi-components of alloys, heavy metals in industrial effluents and fission products of radioactive elements [72,73]; as well as organic ions and organic compounds that are not ionized at all.

This separation method is based on ion-exchange process occurring between the mobile phase and ion-exchange groups bonded to the support material. In highly polarize ion, additional non-ionic adsorption processes contribute to the separation mechanism. In Inorganic ion-exchange materials, the stationary phase consists of polystyrene, ethylevinylbenzene, or methacrylate series co-polymerized with divinylbenzene and modified with ion-exchange groups.

Inorganic-cation exchangers with much more satisfactory properties have been prepared by combining group IV oxides with the more acidic oxides of group V and VI. For example, Zirconium Phosphate with variable ZO_2:P_2O_3 ratios have been obtained by precipitation with alkali phosphates or phosphoric acid from the solution of Zirconyl chloride. Organic-inorganic ion-exchange materials are the new development of composite ion-exchange materials.

Ion-exchange chromatography is used for the separation of both inorganic and organic amines and cations.

1.3.3 Ion-exchange process and its mechanism

The ion-exchange process became established as an analytical tool in laboratories and in industries, as chiefly practical chemists interested in effects and performance etc studied it. The primary condition of an ion-exchange process is the stoichiometry. In organic resins, it is an established fact [74]. The exchange of ion takes place stoichiometrically, really by the effective exchange of ions between two immiscible phases, stationary and mobile. A typical ion-exchange reaction may be represented as follows:

$$\overline{AX} + B\,(aq) \rightleftharpoons \overline{BX} + A\,(aq) \qquad \text{.....1.1}$$

Where A and B (taking part in ion-exchange) are the replaceable ions, and X is the structural unit (matrix) of the ion-exchanger. Bar indicates the exchanger phase and (aq)

represents the aqueous phase.

In order to describe equilibrium and to understand the mechanism of an ion-exchange process occurring on the surface of exchanger and to evaluate its theoretical behavior, it is important to have a study of its kinetics and thermodynamics. Since inorganic ion-exchangers possess a rigid matrix they do not swell appreciably and hence such studies are simpler to perform on them as compared to the organic resins that swell appreciably. Ion-exchange equilibrium may be described by two theoretical approaches *viz* (i) *Based on law of mass action, and* (ii) *Based on Donnan theory.*

From the theoretical point of view the *Donnan theory* has an advantage of permitting a more elegant interpretation of thermodynamic behavior in an ion-exchanger. Probably, it was the first time when quantitative formation of ion-exchange equilibrium had been made by *Gane* [75] by using the mass action law in its simplest form without involving the concept of activity coefficients. This concept was further accounted by *Kielland* [76] and finally, a suitable choice of general treatment was given by *Gaines* and *Thomas* [77]. Many workers have studied the thermodynamics of cation-exchange on zirconium (IV) phosphate [78-81]. In a series of papers, the effect of crystallinity on the thermodynamics of ion-exchange of alkali metal ions/H^+ ions on the samples of α -zirconium phosphate were examined. Ion-exchange isotherms and calorimetric heats of exchange were determined on samples varying from amorphous to highly crystalline [82-86].

However, from the practical point of view, the mass action approach is simpler. *Nancollas* and *coworkers* [87-89] have interpreted the thermo dynamical functions in term of the binding nature between alkali metals and the ion-exchange matrix. The ion-exchange equilibria of Li(I), Na(I) and K(I) on zirconium (IV) phosphate have also been studied by *Larsen* and *Vissers* [90] who calculated the equilibrium constants and other thermo dynamical parameters *viz.* ΔG^o, ΔH^o and ΔS^o. Similar studies have been made on anion-exchanger also [91]. Ion-exchange equilibria of alkaline earth metal ions on different inorganic ion-exchangers such as tantalum arsenate [92], iron (III) antimonate [93], antimony (V) silicate [94], zirconium (IV) phosphosilicate [95,96] and alkali metal ions on iron (III) antimonate [97] and α -cerium phosphate [98]. Other interesting thermodynamic studies relate to the adsorption of pesticides on inorganic and composite ion-exchangers have also been studied in these laboratories [99,100]. The study has revealed that the adsorption is higher at lower temperature and the presence of an ion-

exchange material in soil greatly enhances its adsorption capability for the pesticides. *Nachod* and *Wood* [101] have made the first and detailed attempt on kinetic studies of ion-exchange. They have studied the reaction rate with which ions from solutions are removed by solid ion-exchangers or conversely the rate with which the exchangeable ions are released from the exchanger. Later on *Boyd et al.* [102] have studied the kinetics of metal ions upon the resin beads and have given a clear understanding about the particle and film diffusion phenomenon that govern the ion-exchange processes. The former is valid at higher concentrations while the later at lower concentrations. *Reichenberg* had studied the kinetic of metal ions on sulphonated polystyrene. Who again, confirmed that at high concentrations the rate is independent of the ingoing ion (particle diffusion); while at low concentrations the reverse is true (film diffusion).

1.4 Organic-Inorganic' Composite Ion-Exchange Materials

Composite materials formed by the combination of organic polymers and inorganic materials are attractive for the purpose of creating high performance or high functional polymeric material termed as "organic-inorganic hybrid materials" [103-116]. The conversion of organic ion-exchange materials into hybrid ion exchangers is the latest development in this discipline. The preparation of hybrid ion-exchangers [117-128] is carried out by the binding of organic polymers i.e. polyaniline, polyacrylonitrile, polystyrene etc. These polymer based hybrid ion exchangers showed an improvement in a number of properties viz chemical, mechanical, radiation stability, improvement in ion-exchange properties and also selective nature for the heavy toxic metal ions. One of the important properties of them is granulometric nature that makes it more suitable for the application in column operations. Hybrid ion exchangers can be prepared as three-dimensional porous materials in which layers are cross linked or as layered compounds containing sulphonic acid, carboxylic acid or amino groups [129]. Some of the hybrid ion-exchangers prepared so far are pyridinium-tungstoarsenate [130], zirconium (IV) sulphosalisylo phosphate [131,132], styrene supported zirconium phosphate [133]. Recently, some organic-inorganic composite ion-exchange materials have been developed in these laboratories. *Khan et al.* have reported polypyrrole Th(IV) phosphate [134], polyaniline Sn(IV) phosphate [135] polyaniline Sn(IV) arsenophosphate [136], Polystyrene Zr(IV) tungstophosphate [137], poly-o-toluidine Th(IV) phosphate [138],

poly-o-anisidine Sn(IV) phosphate [139], poly-o-toluidine Zr(IV) phosphate [140], and polypyrrole/polyantiminc acid [141], used for the selective separation of Pb^{2+}, Hg^{2+}, Cd^{2+}, Hg^{2+}, Hg^{2+}, respectively, and ion-exchange kinetics of M^{2+}-H^{+} exchange and adsorption of pesticide [142], have also carried out on these materials. *Beena Pandit et al.* have synthesized such type of ion-exchange materials, i.e. o-chlorophenol Zr(IV) tungstate and p-chlorophenol Zr(IV) tungstate [143] pectin based Th(IV) phosphate [144], with great analytical applications have been investigated by *Varshney et al.* These materials can be used as ion-exchange membranes and ion selective electrodes [145,146].

1.5 Electrical Properties of Materials

Consideration of the electrical properties of materials is often important when materials selection and processing decisions are being made during the design of a component or structure. The electrical behaviors of the various materials are divers.

Some need to highly electrically conductive, whereas electrical insulativity is required of others. In order to explore the electrical properties of materials, that is, their responses to an applied electric field, it is necessary to discuss the phenomenon of electrical conduction: the parameters by which it is expressed, the mechanism of conduction by electrons, and how the electron energy band structure of material semiconductors, and insulators. Nowadays, particular attention is given to the characteristics of semiconductors.

1.5.1 Electrical conduction in materials

Electrical conductivity (σ) used to specify the electrical character of a material. It is simply the reciprocal of the resistivity, or

$$\sigma = \frac{1}{\rho} \qquad \text{.....1.2}$$

and is indicative of the ease with which a material is capable of conducting an electric current. Materials show electrical conduction due to the movement of charge carriers on application of volatage as given by the equation

$$\sigma = qn\mu \qquad \text{.....1.3}$$

Where σ is electircal conductivity of material, n is the number of charge carriers, q is the charge and μ is drift mobility of charge carriers. Drift mobility characterizes the ease

with which the charge carriers can move under the influence of applied material. Electrons and holes in the electronic contribute and cations in ionic conductors. Mechanisms that have been employed to explain the electrical conduction in materials, include ionic conduction, band type conduction, hopping and excitonic conduction, quantum mechanical tunneling between metallic domains etc.

1.5.2 Electrically conducting materials

The ability of materials to conduct electricity varies widely allowing their classification into good conductors (metals), semiconductors and non-conductors (insulators). Another classification of solids may be based upon the number of current carriers (electrons). A conductor has a large number current carriers and this number is independent of temperatures. An insulator has relatively few numbers of current carriers at ordinary temperatures and semicondutor has current carries, the number of which in particular material depends on the temperature. We already know that electrical conductivity is one of the most important properties of metals. Silver has the highest electrical conductivity. Copper comes next and is similar to silver from the point of view of atomic structure. Aluminium, which is light and has a high conductivity, is rapidly becoming more important as a conductor material. Gold which has conductivity higher than that of aluminium but lower than that of silver or copper do not find use in electrical industry because of it is expensive. The resistivity of metallic conductors at room temperature lies between 1.6×10^{-6} to 100×10^{-6} ohm cm^{-1} and that of insulators between 10^{9} to 101^{8} ohm cm^{-1}. The corresponding value for semiconductors is intermediate between those for conductors and insulators. It is the order of 0.01-50 ohm cm^{-1} at room temperature. The resistivity of semiconductors is considerably more sensitive to changes in temperature than is the case for metals. As a result compact temperature measuring instruments using semiconducting thermal resistors may be constructed. At high temperatures, the number of current carriers in a semiconductor is fairly large while at low temperatures this number is relatively small. The number of current carriers in semiconductor however is many orders of magnitude smaller than in a conductor.

K. Onnes first oserved superconductivity in 1911; on cooling a sample of mercury below 4.2 K the resistivity of the metal suddenly decreased to an immeasurably small value. Since then many metal and their alloys, many compounds which have zero resistance below a certain critical temperature; T°.

1.5.3 Electrically conducting polymers

Polymers have traditionally been utilized in electrical and electronic applications in view of high resistivity (their electrical conductivity lies in the range of 10^{-11} to 10^{-18} Scm $^{-1}$) and excellent dielectric properties. Research and development have demonstrated the possibility of obtaining polymers with almost properties typical of any structural material, semiconductor or metal. However, due to the electrical insulating properties, polymers remain unsuccessful in replacing metals and semiconductors in electrical and electronic applications. To improve gas sensors characteristics, novel sensitive organic layers, electronic conducting polymers were developed. Now the electrically conducting polymers are establishing their place as the central constituents of various electronic and photonic systems. The award of the *Nobel Prize* has recognized the interest of these materials for the year 2000 in Chemistry to *Heeger* [147], *MacDiarmid* [148] and *H.Shirakawa,* who synthesized the first conducting polymers and proved their potentialities in a large number of applications. The first account of observation of the electrical conductivity was reported in 1800s when it was seen that by incorporation of carbon black, the conductivity of natural rubber could be enhanced. The combination of electronic and optical properties of the semiconductors with the mechanical properties and the processibility of the polymers makes conjugated polymers rather unique and potentially useful for a wide array of applications. Conjugated polymers such as polyacetylene, polyphenylene, polythiophene, polypyrrole, polyaniline etc. possess a backbone that can produce, sustain and assist the motion of charge carriers in the from of electrons or holes.

1.5.4 Electrically conducting 'organic-inorganic' composites

The conjugated backbone of electrically conducting organic polymers is responsible for their electroactive character and, therefore, possesses good tunable electrical conductivity as well as electrochromic properties [149-152]. But they are chemically sensitive and have poor mechanical properties and pose processibility problems. The inherent instability is also due to highly unsaturated backbone of conjugated polymers. Stability problems have, therefore, caused many research groups to search for conjugated polymers of high stability. To meet the demand of materials of improved performance, explosive research is going on to synthesize the composites (combinations of desirable properties of each component) of 'organic-organic' and 'organic-inorganic' nature. In the view of the

above-mentioned facts, researchers have shown much interest in the study of electrically conducting behavior of 'organic-inorganic' composite materials [153-157]. Special interest today is focused on composite system having high conductivity at ambient and sub-ambient temperatures, since they find unique application, such as separators in high power and rechargeable lithium batteries. Moreover, composite materials composed of oxides or polyvalent metal acid salts and conducting polymers have brought out more fields of application, such as smart windows, toners in photocopying, conducting paints etc. [158-160].

1.6 Sensors

Organic or inorganic semiconductors have been reported to change their conductivities when exposed to variety of organic and inorganic vapors. Thus, these materials can be expected to behave as sensors. Composite materials of tin oxide and derivatives of polypyrrole [161] gave reversible changes in electrical resistance at room temperature when exposed to a variety of organic vapors. Composite materials containing 2.5% polymer by mass were fabricated and exposed to low concentrations of ethanol, methanol, acetone, methyl acetate and ethyl acetate vapors [162-165], the composite materials were found to give more significant and reversible decrease in electrical resistance in comparison with sensors constructed solely of tin dioxide or polypyrrole. These materials could be used in the quality control of foodstuff, especially in the early detection of soft rot in Potato tubers. Some researchers incorporated preformed polypyrrole and poythiophene into clay (montmorillonite) by the interaction of colloidal nanoparticles of the polymers with the colloidal layered host [166]. This method using a colloid-colloid reaction [167] might provide a general route to incorporation intractable polymers within layered host structures that can be exfoliated, such as smeccice clays [168], metal disulfides and some metal oxides. These composite materials have potential to be used as hybrid sensors. Chemical sensing properties of the electrochemically prepared polypyrrole- poly (vinyl alcohol) (Ppy-PVA) films were studied by exposiing them to NH_3 gas.

1.7 Membrane an Introduction

A precise and complete definition of the word "*Membrane*" is difficult to make, and any complete definition given to cover all the facets of membrane behavior will be

incomplete. According to *Sollner* [169] a membrane is a phase or structure interposed between two phases or compartments which obstructs or completely prevents gross mass movement between the later, but permits passage, with various degree of restriction of one or several species of particles from one to the other or between the two adjacent phases or compartments, which thereby acting as a physico-chemical machine transforms with various degree of efficiency according to its nature and composition of the two adjacent phases or compartment. In simple terms, it is described as a phase, usually heterogeneous, acting as barrier to the flow of molecular and ionic species present in the liquids and for vapors containing two surfaces. The term heterogeneous has been used to indicate the internal physical structure and external physico-chemical performance [170-172]. From this point of view, most of the membranes in general are to be considered heterogeneous, despite the fact that, conventionally, membranes prepared from coherent gels have been called homogeneous [173].

The usefulness of a membrane in a mass separation process is determined by its selectivity, by its chemical, mechanical and thermal stability and its overall mass transport rate. The chemical nature of the membrane material is of prime importance when components with more or less identical molecular dimensions and similar chemical or electrical properties have to be separated. The chemical, mechanical and thermal stability of the membrane determines to a large extent its useful lifetime, especially when the feed solution contains strong solvents, strong oxidants and extremely low or high pH values, when the process has to be carried out at elevated temperatures or when frequent cleaning procedures of the membrane are required. The mechanical properties of a membrane are of special significance in pressure driven process such as reverse osmosis, ultra filtration, *etc.* Ideally, a membrane should not change its useful properties when it is derived out or when the composition of feed solution is changed drastically. For economic reasons, finally the flow rate of the permeable components through a given membrane area under a given driving force should be as high as possible to minimize investment costs which are generally proportional to the membrane area installed to give a certain process capacity. To significantly expand the use of membranes in mass separation processes beyond their present applications, membranes with more specific transport properties, longer lifetimes and higher flux rates are required.

1.8 Ion-Selective Electrodes

Ion-selective electrodes are mainly membrane-based devices; consist of perm-selective ion-conducting materials, which separate the sample from the inside of the electrode. On the inside is a filling solution containing the ion of interest at a constant activity. The membrane is usually non-porous, water insoluble and mechanically stable. The composition of the membrane is designed to yield a potential that is primarily due to the ion of interest (via selective binding processes, *e.g.* ion-exchange, which occur at the membrane-solution interface). The purpose is to find membranes that will selectively bind the analyte ions, leaving co-ions behind. Membrane materials, possessing different ion-recognition properties, have thus been developed to impart high selectivity.

The Ion-Selective Electrodes (ISEs) are commonly known as "Ion Sensors" or "Electrochemical Sensors". The history of ion-selective electrodes in the past decade shows the typical behavior of expansion followed by consolidation. The rapid growth of new electrodes for ion activity measurement, new formats and new material of construction has given a way to more in prospective research on "How and Whys" of the functioning of various electrodes and extensive application studies, uses of ISEs as instrumental components and in diverse field, particularly in clinical and environmental chemistry.

1.8.1 Physico-chemical properties of ion-selective electrodes

In order to study the characteristics of the electrode, the following parameters were evaluated: electrode response or membrane potential, lower detection limit, slope response curve, response time, working pH range, *etc.*

1.8.1.1 Electrode response or membrane potential

The use of ion-selective electrodes depends on the determination of potentials [174,175]. The potentials cannot be determined directly but can be easily derived from the e.m.f. Values for the complete electrochemical cells which comprise the membrane separating solutions 1 and 2 as well as the two reference electrodes when the ion exchange membrane separates two solution 1 and 2 both containing the same counter ion or A, a membrane potential (E_m) is developed across the membrane due to the diffusion of counter ions from the higher to the lower concentration. The membrane potential is expressed in equation (1.4):

$$E_m = \frac{RT}{Z_A F}\left[\ln\frac{[a_A]_2}{[a_A]_1} - (Z_y - Z_A)\int_1^2 t_y d\ln a\pm\right] \quad \text{.....1.4}$$

Where A = counter ion, Y = co-ion, Z = charge on ions, t_Y = transference number of co-ions in the membrane phase, $[a_A]_1$ and $[a_A]_2$ = activities of the counter ions in the solution 1 and 2, $a_\pm$ = mean ionic activity of the electrolyte. It is quite evident from the equation that 'E_m' is the sum of diffusion and *Donnan Potential.* In equation (1.4) the right hand side consists of two terms, the first term represents the thermodynamic limiting value and the second term denotes the diffusion potential due to co-ion flux membrane. If the membrane is considered to be ideally perm-selective membrane (t_y = 0) then equation (1.4) takes the form of the well-known *Nernst Equation* as follows:

$$E_m = \pm\frac{RT}{Z_A F}\ln\frac{[a_A]_2}{[a_A]_1} \quad \text{.....1.5}$$

The equation (1.5) simply represents *Donnan potential* for an ideally perm-selective membrane or it can be said that it gives the thermodynamic limiting value of concentration potential. Equation (1.5) takes positive sign for cations and negative sign for anions. The membrane potential measurement is carried out using a cell set up of the following type:

Solution 2				**Solution 1**
External Saturated Calomel Electrode (SCE)	Test or External Solution	Membrane	Internal Solution	Internal Saturated Calomel Electrode (SCE)
$E_L(2)$				$E_L(1)$

In general practice, the concentration of one of the solution (say 1) is kept constant (usually 0.1 M) and this solution is referred as internal or reference solution and a SCE is dipped in this internal solution as an internal reference electrode. The membrane together with internal solution and internal reference electrode is one compact unit, which as whole is called as membrane electrode. This membrane electrode is then immersed in solution 2,

usually referred as external solution or test solution, having an external reference electrode. The e.m.f. of this potentiometric cell is given by the following expression:

$$E_{cell} = E_{SCE} + E_{L(2)} + E_m + E_{L(.)} - E_{SCE} \quad \text{.....1.6}$$

where E_{SCE}, E_L and E_m refer to Calomel Electrode, junction and membrane potentials, respectively. On combining equation (1.5) and (1.6), the following equation takes the form-

$$E_{cell} = E_{SCE} - E_{SCE} + E_{L(2)} + E_{L(1)} \pm \frac{RT}{Z_A F} \ln \frac{[a_A]_2}{[a_A]_1} \quad \text{.....1.7}$$

For cation-exchange membrane,

$$E_{cell} = E_{L(2)} + E_{L(1)} - \frac{RT}{Z_A F} \ln [a_A]_1 + \frac{RT}{Z_A F} \ln [a_A]_2 \quad \text{.....1.8}$$

As the activity of internal solution is kept constant and the values of $E_{L(1)}$ and $E_{L(2)}$ are also almost constant, the term in parenthesis may be taken equal to a constant, E^o. Furthermore, the values of $E_{L(1)}$ and $E_{L(2)}$ are negligible (due to salt bridge in use), the cell potential in above equation may approximately be taken as membrane potential. The equation (1.8) reduces to-

$$E_{cell} = E^o + \frac{RT}{Z_A F} \ln [a_A]_2 \quad \text{.....1.9}$$

Now, it is quite clear from equation (1.9) that the cell potential would change with the change in concentration (or activity) of the cation in external or test solution 2. At 25 °C, value of RT/Z_AF comes out to be $0.059/Z_A$ volts. The membrane is said to give Nernstain response if the slope of a plot between cell potential and log activity comes out to be $0.059/Z_A$ volts. These plots are called Nernst plots and the slope as Nernstian slope. From the calibration graph, it can be observed that the response curve is linear down to a particular concentration after which the curve tends to become parallel to the x-axis. Suitable concentrations were chosen corresponding to the sloping portion of the linear curve for the measurement of potentials. The slope of this linear curve is important and

tells whether the electrode response follows the Nernstian response or not. A potentiometric sensor is said to be behaving in a Nernstian or close to Nernstian fashion, if the slope is ±1-2 mV of the theoretical value. Below this range, it is sub-Nernstian and above it, it is hyper-Nernstian. Sensors, which are outside the Nernstian range, can still be useful analytically.

1.8.1.2 Selectivity coefficients

A selectivity coefficient is one of the most important factors of ion-selective electrodes (ISEs), on the basis of which the potential application of an electrode in a given system can be predicted. Generally, ISEs are mainly membrane-based devices, consisting of perm-selective ion-conductive materials, which separate the sample from the inside of the electrode. Inside the electrode, a filling solution containing the ion of interest at a constant activity is taken into consideration. The membrane is usually non-porous, water-insoluble and mechanically stable. The composition of the membrane is designed to yield a potential that is primarily due to the ion of interest. The purpose is to find membranes that will selectively bind the analyte ions, leaving co-ions behind. Thus, membrane materials, possessing different ion-recognition properties, have been developed to impart high selectivity. Detailed theory of the processes at the interference of these membranes, which generate the potential, is available elsewhere [176-178]. Such a potential arises whenever the membrane separates two solutions of different ion activities. The resulting potential of the ion-selective electrode, which reflects the unequal distribution of the analyte ions across the boundary, is generally monitored relative to the potential of the reference electrode. Since the potential of the reference electrode is fixed, the measured cell potential reflects the potential of the ISE, and can thus be related to the activity of the target ion. Ideally, the response of the ISE should obey equation (1.10):

$$E = E^{0} + (2.303\ RT/Z_i f) \log a_i \qquad \text{.....1.10}$$

However, equation (1.10), has been written on the assumption that the electrode responds only to the ion of interest, '*i*'. In practice, no electrode responds exclusively to the ion specified. The actual response of the electrode in a binary mixture of the primary and interfering ions ('*i*' and '*j*', respectively) is given by the *Nikoloskii-Eisenman* equation:

$$E = E^{o} + (2.303\ RT/Z_i f) \log (a_i + K_{ij}^{pot} a_j^{Z_i/Z_j}) \quad \text{.....1.11}$$

Where E = potential of the electrode, E^{o} = standard potential of the electrode, a_i = activity of '*i*' ions, a_j = activity of '*j*' ions, Z_i = charge on the '*i*' ion, Z_j = Charge on the '*j*' ion, K_{ij}^{pot} = selectivity coefficient of the electrode in the presence of *j* ions, which measure the relative affinity of ions '*i*' and '*j*' towards the ion-selective membranes.

No electrode is absolutely selective for a particular ion. Thus, the selectivity of the electrode depends on selectivity coefficients. The lower the value of K_{ij}^{pot}, the more selective is the electrode. For ideally selective electrodes, the K_{ij}^{pot} would be zero. So, it is important for the analytical chemist to realize the importance of selectivity coefficient of a particular electrode. The inconsistent values of selectivity coefficient may cause problems [179-181]. Various methods [182] have been suggested for determining the selectivity coefficient, however, it falls in two main groups, namely- (1) Separate-solution method and (2) Mixed-solution method.

Separate-solution methods [183-185]: In the separate-solution method, the potential of the electrode E_i and E_j are measured separately in solutions containing '*i*' only of activity a_i (no '*j*' present) and '*j*' only of activity a_j (no '*i*' present), respectively and are given by the following equations:

$$E_i = E^{o} + (2.303\ RT/Z_i f) \log a_i \quad \text{.....1.12}$$

$$E_j = E^{o} + (2.303\ RT/Z_i f) \log K_{ij}^{pot} a_j \quad \text{.....1.13}$$

K_{ij}^{pot} can be calculated either with the so-called equal activity or with the equal potential method. In both cases, it is tactually assumed that the electrode standard potentials are equal in the presence of ion '*i*' as well in that of ion '*j*' and also that the response is Nernstain for both ions. According to the method of equal activities the solution of ion '*i*' and '*j*' are prepared at the same concentration and the potentiometric measurements are carried out. From the equations (1.12) and (1.13), we get

$$\log K_{ij}^{pot} = \frac{E_j - E_i}{2.303RT/Z_i F} + \log \frac{a_j}{(a_j)^{Z_i/Z_j}} \quad \text{..... 1.14}$$

The term $2.303RT/Z_iF$ is the slope of Nernst plot. As most of the solid membranes exhibit deviation from Nernstian behaviour, the experimental slope (S), usually differs from the theoretical slope *i.e.*, $2.303RT/Z_iF$. Thus, it is a practice to use 'S' instead of Nernstian slope for the calculation of K_{ij}^{pot}. As such equation (1.14) takes the form.

$$\log K_{ij}^{pot} = \frac{E_j - E_i}{S} + \log \frac{a_j}{(a_j)^{Z_i/Z_j}} \qquad \text{.....1.15}$$

Thus, using equation (1.15) selectivity coefficient K_{ij}^{pot} can be calculated. The separate solution technique for determining selectivity coefficients is simple and allows a number of K_{ij}^{pot} values to be measured on the basis of different activities and potentials.

Mixed solution methods [186-192]: In the mixed solution techniques, the electrode potentials are measured in solutions containing both the primary ion '*i*' and the interfering ion '*j*'). The procedure for determining selectivity coefficients by Mixed Solution Method is.

Procedure In this procedure, the potentials of the electrode E_i and E_{ij} are measured in solutions of primary ion '*i*' only and a mixture of primary and interfering ion '*j*', respectively.

$$K_{ij}^{pot} = \log [10^{(Ei+j - Ei/m)} - 1] + \log a_i - Z_i/Z_j \log a_j \qquad \text{.....1.16}$$

Or, in other form, it can be writen as

$$K_{ij}^{pot} = \frac{a_j}{a_j^{Z_i/Z_j}} \left[\left\{ 10^{\frac{E_{i+j} - E_i}{2.303RT/Z_iF}} \right\} - 1 \right] \qquad \text{.....1.17}$$

1.8.1.3 Response time

Another important factor besides linear response that recommends the use of ISEs or membrane electrode is the promptness of the response of the electrode. The response time of an ion-selective electrode is the time needed to attain equilibrium value (*i.e.* to obtain a steady potential) within ±1 mV after a ten-fold increase or decrease in the concentration of the test-solution. However, the interpretation of response time varies from a group of workers to others. *Punger et al.* [193-197] have discussed this aspect in details.

1.8.1.4 Effect of pH

The membrane electrodes with polymer binders like PVC do response to change in the pH value of the solutions. So it is necessary to study the effect of pH and the favorable working range of pH has to be evaluated for accurate measurements. Since in membrane electrodes one or other polymeric binder was used for the construction of the membrane, it is necessary that one finds out the effect of pH on the electrode response. The electrode could be safely used for measurements of their ions provided the pH of the solutions used falls in the range where the electrode response does not change with the pH, and this pH range is used as working pH range of the electrode.

1.8.1.5 Life span of membrane electrode

Ion-exchanger membrane electrodes can be used for one to three months in continuous service. This short lifetime may be related to the gradual loss of the ion- exchanger through the porous membrane. The membrane, internal filling solution and the ion-exchanger are replaced when the electrode response becomes noisy or drifts. So, in order to find out the life time of the electrode, the electrode response were noted every week and response curve is drawn for the data usually at the initial period some changes in the response are noted *vis-à-vis* the slope of the response curve but after the week or so, the electrode response remains fairly constant over a period of time after this period the electrode starts behaving erratic, therefore cannot be used for any measurements. This period over which the electrode response is constant can be called a life of electrode.

1.9 Literature Review on Ion-Exchange Membranes and Ion-Selective Electrodes

A large number of ion-selective electrodes using ion-exchangers have been developed during the past 25 years. The literature survey reflects good volume on this topic and it is

very difficult as well as unmanageable to compile all of them here. The research work on these ion-selective electrodes has begun in 1920"s but there systematic studies started after *Pungor et al.* [198,199] in 1961. Therefore, in thus task we have reviewed heterogeneous ion-selective member electrode based on inert binder PVC and polystyrene selective for alkali, alkaline earth metals and heavy metal ions Research in the field of ISEs was enormously stimulated by the publication by *Fran and Roos* [200,201] of there article on the floride and calcium ion-selective electrode. A number of review articles [202-211] have come across from time to time towards the work done by various eminent persons.

An epoxy resin (*e.g.* Araldite) first used by *Coetzee et al.* proved to be the most suitable and widely used material. They have worked on thallium(I) heteroployacid salt-epoxy resin membranes in their studies and they also have determined Cs^+ potentiometrically [212,213]. Tungstoarsenate based ion-selective membranes have been developed by *Malik et al.* [214] and found very much suitable in the determination of Cs^+ and Tl^+ ions. However, there has been only a few reports concerning Thallium(I) ion-selective membrane electrode [215-224]. They need to improved with regard to there low selectivities against alkali metal ions linearity and pH-dependance.

There has been widespread interest in developing ion-selective electrodes (ISEs) for determining alkaline earth metals, as they exist in diverse samples. Amongst the alkaline earth metals, most investigated and developed ISEs are Ca^{2+}-selective electrodes. The first Ca^{2+}-selective electrode was a liquid membrane electrode developed by *Ross*. It was prepared by using a liquid membrane of didecyl -phosphate in di-n-octyl phosphonate. The useful Ca^{2+}-selective electrodes were developed by *Thomas, Moody* and *coworkers* [225-227] by incorporating Ca-bis[2,6-dinitro-4-(1,1,3,3-tetramethylebutyl)] phenoxide and Ca-bis[di{4-(1,1,3,3-tetramethylbutyl) phenyl}] phosphate in PVC. *Chattopadhyaya* and *Misra* [228] reported the Ca^{2+}-selective heterogeneous precipitate based membrane using Ca(II) rhodizonate as the electroactive material. The electrode was used as an indicator electrode in the precipitation titration of $CaCl_2$ with $Na_2C_2O_4$.

Little work has been done on the developments of ISEs for two alkaline earth metal ions, Mg^{2+} and Sr^{2+}. Only few such electrodes are reported which show interference to other alkaline earth metal ions. Recently, an electrode prepared using a membrane of phenylene bis(ditolylphosphineoxide) in PVC was reported as Mg^{2+}-sensor. The electrode

shows good selectivity towards Mg^{2+} over Ca^{2+} and works well in the concentration range 6.0 x 10^{-5}- 1.0 x 10^{-1} M. Another electrode for Mg^{2+} has been developed by *O'Donnell* and *coworkers* [229] using various octamethylene bis(malonic acid diamides) and tris(malonic acid diamides) in PVC with 2-nitrophenyloctyl ether as solvent mediator.

First useful Sr^{2+} ion-selective electrode was developed by *Baumann* [2310] using strontium complex of polyethylene glycol as electro active material. The electrode was selective towards Sr^{2+} over Ca^{2+} and other bivalent cations with the exception of Ba^{2+} and Hg^{2+}. *Srivastava* and Jain [231] have reported a heterogeneous membrane using hydrous thorium oxide embedded in polystyrene while *Jain et al.* [232] have used strontium tungstoarsenate in araldite for Sr^{2+}-selective electrodes. The membrane electrode has been used as an end point indicator in the potentiometric titration involving Sr^{2+} ions against diammonium hydrogen phosphate.

Ba^{2+}-selective polymeric membrane electrodes have been constructed from lipophilic electrically neutral carriers [233] and neutral carboxylic poly ether antibiotic [234,235] and have been found suitable for the titration of Ba^{2+} in non-aqueous media as well as for the determination of SO_4^{2-} in the combustion products. The membranes of benzo-15-crown-5 and its Ba-complex prepared by using an epoxy resin binder were also found suitable as Ba^{2+}-sensor [236]. These electrodes show good selectivity for Ba^{2+} and also used for the titration of Ba^{2+} against SO_4^{2-}.

Chelating ion-exchanger resins are found to possess specific selectivity for some metal ions and play an important role in separation processes. *Srivastava et al.* have reported the utility of salicylaldoxime-formaldehyde resin membranes for the estimation of Zn^{2+}. Recently *Wardak et al.* [237] studied the properties on the ion selective electrode with a chelating pseudo-liquid membrane phase for Zn^{2+} determination. Cu(II) is an essential element and is also toxic at elevated concentration. Its reactivity and biological uptake are strongly influence by the free ion concentration that is controlled by the extent of copper complexation with ligands. Potentiometric measurements with a Cu^{2+} ion-selective electrode allow directly determining free ion concentration in water samples. For copper determination, solid membrane electrodes based on copper sulfide, tungsten oxide, ion-exchangers and copper (III) complexes as electro active material have been tried as copper potentiometer sensors.

In measuring the heavy metals ions like Cd^{2+} in the industrial wastewater, the ion-selective electrodes are very convenient because of simplicity and selectivity. *Ross et al.*

[238,239] have reported the precipitate based solid state CdS-Ag_2S mixture membrane by stoichiometric reaction. Also *Hirata et al.* [240] have developed the ceramic solid-state CdS-Ag_2S mixture membrane by baking the CdS-Ag_2S mixed powder or its pressed membrane at 700 °C. *Hopertenam* and *Cosma* [241] have reported some preparation methods for mixtures of cadmium and silver sulfides with Cd^{2+}-selective electrode properties. Sodium sulfide, thioacetamide and sodium thiosulfate were used for simultaneous precipitation of CdS and Ag_2S.

Srivastava et al. [242] have reported an elasticized PVC based membrane of benzo-15-crown-5, which exhibited a good response for Cd^{2+} in a wide concentration range ($3.16 \times 10^{-5} - 1.00 \times 10^{-1}$ M) with a slope of 20 mV/decade of Cd^{2+}. The electrode was used at one stretch, for a period of 2 months and is played good selectivity for Cd^{2+} over alkali, alkaline earth and transition metal ions. The membrane sensor was also used as an indicator electrode in potentiometric titration involving Cd(II) ions.

Because of the increased industrial use of lead, at one hand and its serious hazardous effect to human health, on the other [243] , the electrochemical properties and preparation of the Pb(II) ion-selective membrane electrodes have been extensively studied by using different active materials. *Thind et al.* [244] have developed Pb^{2+} ion-selective membrane using lead antimonate as an electroactive phase and araldite as a polymer binder.

Gupta et al. [245] have published their results on the studies of araldite based Zr(IV) tungstophosphate (ZWP) membrane as Pb(II) ion-selective electrode. *Tavakkoli* and *Shamsipur* [246] had reported a Pb-ISE based on dibenzopyridino-18 crown-6 as membrane carrier. This lead selective electrode exhibited comparatively good selectivities with respect to alkali, alkaline earth and some transition and heavy metal ions. Recently, *Malinowska et al.* [247] have reported a lead selective membrane electrode containing ionophores based on diaza-18-crown-6 units possessing amide and sulfonamide functions. *Ganjali et al.* have reported a PVC membrane electrode for Pb^{2+} ion based on recently synthesized dimethylbenzotetrathiafulvalene as membrane carrier. The electrode has found a very low limit of detection of 8×10^{-6} M and can be used as an indicator electrode in potentiometric titrations of Pb^{2+} ions in both H_2O and 90% MeOH solutions. *Ensaf et al.* [248] have prepared the lead(II)-selective membrane electrode by incorporating cryptand as the neutral carrier into a plasticized PVC membrane. The electrode was used as an indicator electrode in the potentiometric titration of Pb^{2+} with EDTA.

Jain et al. and Srivastava et al. have also fabricated polystyrene supported heterogeneous ion-exchange membrane electrode of heteropolyacid salts (*e.g.* Ce(IV) selenite) which were found to be selective for Hg^{2+}. Recently, *Abbas et al.* have reported a new triiodomercurate-modified carbon paste electrode for the potentiometric determination of Hg(II) ions. Potentiometric determination of Hg(II) was also reported by some other workers .

A less attention has been made for determining tripositive metal ions. Very few potentiometric devices have been designed for aluminum. Recently, *Saleh et al.* have reported a novel potentiometric membrane sensor for selective determination of Al(III) ions. This electrode has a minimal interference of Pb^{2+} and Hg^{2+} ions and successfully applied for the potentiometric titration of HPO_4^{2-} with Al^{3+} and for direct potentiometry of Al^{3+} content of some rock samples.

Khan et al. [249-254] have published their findings for the determination of Hg(II), Cd(II), and Pb(II), by potentiometric titration using polypyrrole/polyantimonic, polyaniline Sn((IV) tungstoarsenate, polyaniline Sn(IV)arsenophosphate, polypyrole Th(IV) phosphate, polyaniline Sn(IV) phosphate, poly-o-toluidine Th(IV) phosphate, poly-o-toluidine Zr(IV) phosphate electrically conducting organic-inorganic composite based ionselective membrane electrodes.

Khan et al. have been reported poly-o-toluidine Th(IV)phosphate [249]; polyaniline Sn(IV) phosphate [250]; polyaniline Sn(IV) tungastoarsenate [251]; Poly-o-toluidine Zr(IV) phosphate [252]; Nylone-6,6 Sn(IV)phosphate [253]; poly-o-anisidine Sn(IV)arsenophosphate [254] based ion selective membrane electrode for the potentiometric determination of Hg(II), Pb(II), Cd(II), Hg(II), Hg(II) and Pb(II), respectively. Ion-selective electrodes for determination of organic ammonium ions were reported by *Egorov et al.* [255]. Dibenzo[*e*,*k*]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene has been explored as an electroactive material for the fabrication of a poly(vinyl chloride)-based membrane electrode for selective determination of Ni^{2+} ions by *Singh et al.* [256]. A highly Ce(III) ion- selective poly vinyl chloride (PVC) membrane sensor based on *N*□-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (NHMF) as an excellent sensing material is successfully developed by *Zamani et al.* [257]. A series of recently synthesized benzo- and pyridine-substituted macrocyclic diamides were studied to characterize their abilities as lead ion carriers in PVC membrane electrodes. The electrode based on 3,15,21-triaza-4,5;13,14-dibenzo-

6,9,12-trioxabicycloheneicosa-1,17,19-triene-2,16-dione by *Kazemi et al.* [258]. Novel platinum(II) selective membrane electrode based on 1,3-bis(2-cyanobenzene) triazene was reported by Gholivand et al. [259]. New silver selective electrode fabricated from benzothiazole calyx(4)arene for the analysis of silver nanoparticles by *Ngeontae et al.* [260]. A new hafnium selective sensor was fabricated from polyvinylchloride (PVC) matrix membrane containing neutral carrier *N,N'*-bis(α-methyl-salicylidene)-dipropylenetriamine (Mesaldpt) as a new ionophore, sodium tetraphenyl borate (NaTPB) as anionic discriminator and dioctyl phthalate (DOP) as plasticizing solvent mediator in tetrahydrofuran solvent by *Rezaei et al.* [261]. Oxalate-selective electrode based on the complex 2,2'-[1,4-butandiyle bis(nitrilo propylidine)]bis-1-naphtholato copper(II) (CuL) as the membrane carrier was developed by *Ardakani et al.* [262]. Mercury ion-selective membrane electrodes based on 2-amino-6-purinethiol (I_1) and 5-amino-1, 3, 4-hiadiazole-2-thiol (I_2) were described by *Gupta et al.* [263]. Mercury(II)-selective polymeric membrane electrode based on the 3-[4-(dimethylamino)phenyl]-5-mercapto-1,5-diphenylpentanone was described by *Xiu Yu et al.* [264].

Some cation-exchangers prepared in our laboratory with their applications are given in Table 1.1 [265-278]

Table 1.1 Some cation-exchange materials prepared in our laboratory with their analytical applications

S. No.	Cation-exchanger	Application	Reference
Inorganic ion-exchanger			
1.	Sn(IV) arsenosilicate	Separation of metal ions	[265]
2.	Zirconium(IV) and Thorium(IV) arsenosilicate	Kinetic studies	[266]
3.	Antimony(V) silicate	Ion-exchange kinetics	[267]
4.	Antimony(V) arsenophosphate	Adsorption of transition metal ions	[268]
5.	Chromium(III) arsenosilicate	Synthesis	[269]
6.	Antimony(V) arsenophosphate	Reverse exchange of alkaline earth metals	[270]
7.	Antimony(V) phosphate	Binary separations of metal ions	[271]
8.	Antimony(V) arsenophosphate	Forward and reverse Na(I)-H(I) and K(I)-H(I)	[272]
9.	Antimony(V) phosphate	Separation of Amino acids	[273]
10	Antimony(V) phosphate	Adsorption of phosphomidon	[274]
11.	Zirconium(IV) tungstophosphate	Synthesis, Hg(II) selective	[275]

Organic-inorganic composite cation-exchanger

1	Polyaniline Sn(IV) Arsenophosphate	Synthesis, ion exchanger behaviour	[276]
2	Tin(IV) arsenophosphate	Adsorption behaviour of carbofuran	[277]
3.	*Zirconium(IV) tungstophosphate*	*Synthesis, ion-exchange behaviour,* Pb(II) selective	*[278]*
4.	Polyaniline Sn(IV) tungstoarsente	Synthesis,, electrically conducting, Cd((II) selective	[137]
5.	Polypyrrole/polyantimonic acid	Synthesis,, electrically conducting, crystalline	[141]
6.	Polypyrrole Th(IV) phosphate	Preparation, electrically conducting and Cd(II) selective	[134]
7.	Polyaniline Sn(IV) phosphate	Preparation, electrically conducting, Hg(II) selective	[135]
8.	Poly-o-toluidine Th(IV) phosphate	Preparation, electrically conducting, nano particle, Hg(II) selective	[138]
9.	Poly-o-toluidine Zr(IV) phosphate	Preparation, nano-composite, electrically conducting, Hg(II) selective	[140]
10.	Poly-o-anisidine Sn(IV) phosphate [POASn(IV)P]	Preparation, electrically conducting, nano-composite, Sb(II) selective	[139]
11.	Nylone-6,6 Sn(IV) phosphate	Synthesis, Hg(II) selective, fibrous	[253]
13	Poly-o-anisidine Sn(IV) arsenophosphate	Synthesis, Pb(II) selective	[254]

1.10 Adsorption

Adsorption is a fundamental natural process. Since the molecules on the surface have an environment different from those in the bulk of material, the surface has a different free energy from the bulk of the material [279]. When the molecules of a gas or liquid are concentrated on the surface of a solid the molecules are said to be adsorbed on the solid surface. This is a surface phenomenon and is different from "Absorption" which is the penetration of one component through the body of another. The material that is adsorbed on to the surface is called the 'adsorbate' and the underlying material as 'adsorbent' or 'substrate'.

Adsorption is sometimes classified as physical and chemical. The physical adsorption is called as "physisorption" and chemical adsorption as "chemisorption". In

the former the molecules are adsorbed on a solid surface by essentially the physical forces. In chemisorption, however, the molecules form the chemical bond with the solid surface. In case of the physical adsorption the Vander Waal's interactions (for instance, dispersion or polar interactions) play an important role between the adsorbent and adsorbate molecules. They are the long but weak interactions. The amount of the energy, when a molecule is physisorbed, is of the order of enthalpy of condensation. This energy can be adsorbed as vibrations of the lattice and dissipated as heat. A molecule bouncing across the surface will lose its kinetic energy and stick to the surface resulting in the rise of temperature of the system i.e. heat is evolved.

In chemisorption, the molecules stick to the surface as a result of the formation of a chemical and usually a covalent bond and tend to find the sites resulting in an increase of the coordination number than in physisorption. In chemisorption the surface enters into reactions as a catalyst. This type of catalysis, called heterogenous catalysis, is understandable only on the basis of some of the informations deduced in adsorption studies. Similar conclusions, that are drawn from the chemical reactions on a surface, help to answer some problems unsolved by adsorption studies. Similar conclusions, that are drawn from the chemical reactions on a surface, help to answer some of the problems unsolved by adsorption studies. The photoelectron spectroscopy (ESCA) can be applied to reveal some of the bonding properties of the adsorbed species. In surface studies this is normally referred as photoemission spectroscopy. Varieties of vibration spectroscopy also reveal the nature of the adsorbed species, and in particular whether the dissociation has occurred. Infrared absorption spectra can be obtained by using infrared transparent materials and a technique that involves the internal reflection.

Adsorption is essentially a phenomenon of separating surface and the interfacial tension [280]. It is generally governed by the thermodynamic relation:

$$\Delta G = \Delta H - T\Delta S \qquad \text{.....1.18}$$

ΔG, ΔH and ΔS are taken, respectively, as the free energy, heat and entropy changes in the process. Since adsorption leads to a decrease in the free energy, ΔG is negative. The adsorbed molecules move from a three dimensional region to a two-dimensional one, which causes a decrease in entropy, i.e. ΔS negative. Thus, ΔH must also be negative, which is usually the case. So, adsorption is generally exothermic.

However, the conditions in solute adsorption are more complicated. Giles et al. [281,282] have reported endothermic adsorption in case of a solute forming large ionic-micelle (e.g. dyes). Josef et al. [283] also found an increase in the isosteric heat of adsorption with an increasing surface coverage in the adsorption of aliphatic amines on alumina. The athermic adsorption covers those cases which do not give measurable heat of adsorption. It is generally the case in ion exchange adsorption of solutes, which do not form large micelles. By definition, the ion-exchange sorption of ions is accompanied by the release of equivalent quantity of ions by the sorbent to the external solution. This distinguishes ion-exchange process from the major sorptive mechanism i.e. physisorption and chemisorption.

1.10.1 Adsorption isotherms

Most of the studies on adsorption from solution have been concerned with equilibrium conditions, and predominantly with the adsorption isotherms. An adsorption isotherm describes the equilibrium relationship between the adsorbed and unadsorbed sample, at a given temperature. It is a plot of the concentration of "X" in the adsorbed phase versus concentration of "X" in the unadsorbed phase. The interest in these isotherms lies in the amount of information they can yield, viz., identification of the adsorption mechanism, heat of adsorption, specific surface area of the porous solid, diagnosis of the orientation of the solute molecules at the surface, and its degree of self-association.

The earlier attempts [284] of classification of isotherms have served for quite a long time. Four types of isotherms are identified on the basis of the shape of the initial part of the isotherm. This classification of isotherms had been reported and theoretically explained by Giles et al. [285] on the basis of solid-solution interface.

(i) Langmuir or L-type isotherms,

(ii) S-type isotherms,

(iii) High affinity or H-type isotherms, and

(iv) Constant partition or C-type isotherms.

The L-type isotherms are most common. They are characterized by an initial region which is concave to the concentration axis. They are obtained when there is no strong competition from the solvent for sites on the surface.

For the S-type isotherms the initial region is convex to the concentration axis which is frequently followed by a point of inflection leading to an S-shaped curve. These isotherms indicate that:

(i) The solvent is strongly adsorbed,

(ii) There is strong intermolecular attraction within the adsorbed layer, and

(iii) The adsorbate is monofunctional.

The second condition is most likely obtained, if the major axis of the adsorbed molecules is perpendicular to the surface. By a monofunctional adsorbate we mean here that the molecule has a single point of strong attachment in an aromatic system or an aliphatic system of more than five carbon atoms. Further, the adsorbate is not miceller. In many cases, the S-curve indicates a 'cooperative adsorption' with solute molecules tending to be adsorbed, packed in rows or clusters.

The H-curve occurs when there is a high affinity between the adsorbate and adsorbent, which is shown even in very dilute solutions. Thus, it can result from the chemisorptions or from the adsorption of polymers or ionic micelles, though other special cases are known.

Finally the C-type isotherm has an initial linear portion which indicates a constant partition of the solute between the solution and the adsorbent and occurs with the microporous adsorbents.

The isotherms have a great utility in diagnosing the mechanism of adsorption, and also in distinguishing the probable configuration of the adsorbed molecules. Thus, S-curve indicates a vertical orientation, L-curve shows the flat orientation and strong intermolecular interaction, while H-type isotherm is assumed to be typical of sample micelle formation. However, such a generalization needs great care, as many other factors also contribute to the isotherm's shape [286].

The adsorbents which have been commonly studied earlier are fly ash [287-292], peat [293-298], fibrous keratinous materials such as wool and hair [299-301], clays [302,303], alumina bauxite [304], woolastonite [305,306], discarded automobile tires [307], suspended particles of river water [308-310] and sludge [311-317]. Some other adsorbents have been proved quite useful viz. alumina, silica, carbon and cellulose [318]. In addition to these, some adsorption studies have also been reported on tin oxide, titanium oxide, thorium oxide and zirconium oxide [319].

The numerous studies on the adsorption of different types of organic and inorganic substances on activated carbon, adsorption of dyes, adsorption of pesticides and pollutants have been done.

1.10.2 Adsorption of pesticides and pollutants

Various adsorption studies of pollutants and pesticides have earlier been carried out on Activated carbon. Yoshitaka et al, [320] studied the effective surface diffusivities of aqueous solutions of chlorinated organics in water on AC using different concentrations. Il'Yasov et al. [321] proposed the mechanism of adsorption using an isothermic model of adsorption. Radeka et al. [322] reported the comparative adsorption behavior of dichloromethane from gaseous and aqueous phases. The adsorption of p-nitroaniline from aqueous solutions by a thick layer of active carbon of varying porous structure and its mechanism was reported by Mamchenko et al. [323].

Lagana et al. [324] studied the behavior of fifty one compounds on graphitized carbon. They determined the sorption capacities and the extent of recoveries for the chlorinated pesticides. The irreversible adsorption of lower aliphatic amines on pure AC surface was studied by Roman et al. [325]. The effect of ph on adsorption of dissolved organic acides, bases, anionic and cationic surface active agents, nonionic organic compounds and polymers from industrial effluents were studied by Wang and Martin [326,327]. The pH effect becomes more significant as the acidity and basicity of the adsorbate in solution increases.

Whitaker et al. [328] has used the isothermal and continuous flow column systems for the adsorption studies of selected pesticides by AC. Lovett and Peltorak [329] reviewed the use of AC for the control of odorous air pollutants. The uses of AC for the treatment of municipal, industrial, and waste waters have been reviewed in detail with a large number of references in literature [330-332]. Janina et al. have removed the benzo(a) pyrene from water by using granular AC. They have observed the Freundlich adsorption isotherm under static conditions [333]. Numerous predictive models [334-341] have been developed to explain the surface and bulk adsorption of organics and inorganics on AC. The behavior of adsorbates and adsorbents, the sites of adsorption, single and multicomponent adsorption and desorption systems were studied and their mechanisms proposed and tested accordingly [342-352].

I. Classification of Pesticides

The pesticides have been classified as follows:

A. Chemical pesticides

B. Biopesticides

A. Chemical pesticides: Chemical pesticides have been classified into three categories:

1. Inorganic pesticides: About A.D. 70 Pliny the Elder recommended that arsenic could be used to kill insects, and the Chinese used arsenic sulphide as an insecticide as early as the late sixteenth century. Other inorganic products used as pesticides contain antimony, boron, copper, fluorine, lead, manganese, mercury, selenium, sulphur, thallium, tin and zinc as their active ingredients. Although these products are not very effective for pesticidal use, many are so persistent in the soil that there are instances as of crops being damaged by their residues in the soil.

2. Organic pesticides: The era of organic pesticides began from 1940. These chemicals are so successful in controlling the pests that there is extremely rapid and general adoption of them and development of new ones. This has progressed so rapidly, that today about 1500 pesticides in the form of 10,000 formulations are in common use around the world.

i. **Organochlorines:** These include DDT, BHC, endosulfan, aldrin, heptachlor, chlordane etc. They are not biodegradable and are persistent in the environment for a long period. They are readily soluble in lipids and even a low concentration of these pesticides may accumulate in the body fat of mammals that might pose problems in the long run. Recommended dose of chlorinated pesticides ranged from 8-10kg per hectare. Organochlorine pesticides persist in the soil for many years and even decades.

ii. **Organophosphates:** These include diazinon, dimecron, dimethoate, malathion, parathion etc. More potent and comparatively less persistent organophosphates have an advantage of having a non-lipophilic nature, moderate persistence, systemic nature and more potency than chlorinated pesticides. They are sparingly soluble in water and biological fluids. They are highly toxic since they inhibit the activity of enzymes. The recommended dose of organophosphates ranged from 4-5kg per hectare.

iii. **Carbamates:** These include carbaryl, carbofuran, baygon, dinocap etc. They are relatively soluble in water. They have reversible mode of action, less persistence, systemic nature and adequate potency against crop pests. Normally they do not

accumulate in tissues and are rapidly excreted when ingested. Thus these were considered to be less toxic than organophosphates.

iv. **Carboxylic acid derivatives:** These include TCA, dalapon, 2,4-D, 2,4,5-T, MCPA etc. They are considered as a potent source of environmental hazards, especially when their degradation products remain active in the environment after desired purpose is over. They are used as herbicides both on agricultural lands and in eradicating weeds in non-productive areas such as roadsides and electric transmission lines.

v. **Substituted ureas:** The substituted ureas such as monuron and diuron form another class of biocides. These are primarily herbicides. Their solubility in water is generally low. They do not create problems of persistence and accumulation due to their facile environmental reactions. These are moderately unstable. These fairly readily undergo dealkylation and dearylation. Therefore, they are of local concern only in the area and period of application.

vi. **Triazines:** The triazines such as atrazine and simazine are used in large quantities as a pre-emergent herbicide in corn fields. Biologically, dealkylation and substitution are the major routes of metabolic breakdown. In soils, dealkylation appears to be the major route. There is a considerable persistence of the resulting products.

vii. **Pyrethroids:** This group includes cypermethrin, deltamethrin and fenvalerate which are commonly used in Indian agriculture. They are very stable in sunlight. These are effective against agricultural pests when used at low rate of 0.1 lb per acre. The recommended dose of pyrethroids ranged from 25-500 g active ingredient per hectare.

viii. **Neem products/Neem based formulations:** The versatile neem tree is a wonder. The limonoids present in it and its products have made it a harmless and useful insecticide, bactericide, fungicide, pesticide etc. It is likely to provide a solution to many of our incurable diseases. Neem crudes such as its kernel crush and oil which are the potential source of bio-actives were formulated as ready to use dust and water dispersible powder and emulsifiable concentrate respectively.

ix. **Others:** These include thiocyanates, dinitrophenols, formamides etc. Thiocyanates have creosote like odours, are relatively safe to use around humans and animals, and give astonishing quick knockdown of flying insects. They interfere with cellular respiration and metabolism. The nitrophenols have been used as ovicides, insecticides, acaricides, herbicides, fungicides and blossom thinning agents. They are quite toxic and their use resulted in several widely publicized deaths. The formamides comprise a very new, small,

but promising group of insecticides. They are used in the control of organophosphates and carbamate resistant pests.

3. **Organic pesticides containing metal ions:** It is a relatively less familiar class of pesticides. The activity of these pesticides depends on the chelating action of the metal ion as well as the activity of the organic matrix.

B. Biopesticides: Biological control of pests or biopesticides has been suggested as an effective substitute for chemicals. It is the control of harmful pests by using other pests, plants or any such living body. The controlling agents include parasites, predators, diseases, protozoa and nematodes that attack pests. Biopesticides are derived from natural materials such as animals, plants, bacteria and certain minerals. For example Canola oil and baking soda have pesticidal applications and are considered biopesticides.

II. Dithiocarbamate Pesticides

Amongst OPCM mentioned above, the heavy metal complexes of dithiocarbamate are well known fungicides. Tisdale first demonstrated the fungicidal possibilities of the dithiocarbamate (thiram) in 1931 in the laboratory of E.I. Du Pont Company, U.S.A. but the commercial production started about a decade later.

It is employed in every use, i.e. contact, protective, eradicative known for fungicides except systemic action. It is widely used on vegetables like lettuce, peanuts, potatoes, tomatoes and brinjals; fruits like apples, figs, grapes, peaches and pears; crops like cotton, maize, paddy and wheat; ornamentals like chrysanthemums, black currants, carnations etc. to control diseases like early and late blight, gall, mildew, leaf spot, rust, scab, smut etc. It is used in seed and soil treatment. It is also known to use as topical ointment to cure dermatophytoses.

As shown in Table 1.2, dithiocarbamates can be divided into two main groups: Group I and Group II. The most noteworthy difference between them being that the members of Group I do not have a H -atom attached to carbamate-N while members of Group II have a H-atom attached to the carbamate- N.

The fungicides of Group I have been further divided into two subgroups:

a. Metal salts or metal complexes of dialkyldithiocarbamic acid e.g. ferbam, ziram
b. Oxidation product of derivatives of dimethyldithiocabamic acid e.g. thiram.

Diethyl analogues of this subgroup are medically used to treat alcoholics.

The fungicides in Group II are ethylene derivatives. Among them, few are salts like metham-sodium, nabam while other are metal complexes like mancozeb, maneb, zineb.

Table 1.2: Classification of Dithiocarbamates

Group	Chemical designation	Types of derivatives
I	Dialkyldithiocarbamate	
		Metal Derivatives
		Na salt (no common name)
		Zn complex (ziram)
		Fe complex (ferbam)
		Oxidation Product
		S – S linkage (thiram)
II	Ethylenebisdithiocarbamate	
		Metal Derivatives
		Na salt (nabam)
		Zn complex (zineb)
		Mn complex (maneb)
		Mixed complex (mancozeb)

D. Applications:

Besides the usage of dithiocarbamate as fungicides the following uses have also been reported in the literature:

a. **Additive in lubricating Oil:** Tanaka et al. [353,354] have reported a process for producing molybdenum oxysulphide dithiocarbamates as lubricant additives. These dithiocarbamates have been found to be good antifriction and anticorrosive agents in lubricating oil. Grobelny et al. [355] have carried nanometric studies of adsorbed layer of zinc di-N-octyldithiocarbamates and di-octylamines used as lubricant additives. Matsuyama et al. [356] have reported that sulphides, dithiophosphates and dithiocarbamates improve oxidation stability of the lubricating oils.

b. **Sulphur vulcanization:** Niewenhuizen et al. [357] have published a review with 262 references describing research methodologies useful in investigating the mechanism of vulcanization and the reactivity of thiuram and dithiocarbamate chemicals. The combined knowledge has been subsequently applied to thoroughly review the mechanism and the chemistry of both thiuram and dithiocarbamate accelerating sulphur vulcanization.

c. **Graft copolymerization:** Kim and Cho [358] have synthesized graft copolymers by iniferter-containing macromer. A monomer such as styrene, methylmethacrylate, ethylacrylate or butylacrylate were copolymerised with chloromethylstyrene by 2,2'-azobisisobutronitrile (AIBN) initiation and the chloride group in the polymer was treated with sodium diethyldithiocarbamate to give dithiocarbamate groups. NMR analysis showed that conversion to dithiocarbamate groups was quantitative for acrylate copolymer as well as styrene copolymer. Graft copolymerization of the macromer such as polystyrene macromer and polymethyl methacrylate (PMMA) macromer yielded graft copolymers.

d. **Chelating agents:** Todorovic et al. [359] have developed pre-concentration method for the determination of trace metals in natural waters using 4-morpholine dithiocarbamate as a chelating agent.

Cesur and Bati [360] have described a method for the pre-concentration of cadmium in water samples by using 1-benzylpiperazinedithiocarbamate (1-BPzDC) as a new reagent, prior to its determination by flame atomic absorption spectrometry (FAAS). This method is based on the fact that cadmium forms cadmium 1-benzylpiperazinedithiocarbamate complex $[Cd(1\text{-}BPzDC)_2]$ in aqueous phase which is extracted with microcrystalline naphthalene on solid phase, then back-extracted with potassium cyanide solution into aqueous phase and measured by FAAS.

Rathore et al. [361] have developed a new precipitation conductometic titration technique for the determination of Zn^{2+}, Pb^{2+}, Hg^{2+}, Hg^{+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, and Fe^{3+} using sodium diethyldithiocarbamate as a titrant.

e. **Chromogenic reagent:** A spectrophotometric method [362] has been reported for the determination of copper (II) using sodium diethyldithiocarbamate as a colouring reagent. The method is based on the formation of a brown suspension of the copper (II) diethyldithiocarbamate which can be extracted with butyl acetate and the coloured extract can be analyzed spectrophotometrically at 560 nm. This method is sensitive to 100 μg of copper (II).

f. **Flotation of non-ferrous metals:** O'Connor et al [363] have used dithiophosphates and dithiocarbamates for the flotation of arsenopyrite. This can be optimized using a two stage flotation process in which a dithiophosphate is added at pH=11 in the first stage and copper sulphate and a dithiocarbamate in the second stage.

Glinkin [364] has published a review with eight references describing the flotation of non-ferrous sulphide minerals with dithiocarbamate reagents. It outlines the use of sodium dimethyldithiocarbamate as a depressor for sphalerite, iron sulphide and S-cyanethyl-N,N/-diethyldithiocarbamate as a collector for copper and molybdenum sulphides. Data pertaining to industrial application of these reagents has been reported.

g. **Ion–Exchanger:**

i. **Analysis of heavy metal ions:** Airoldi et al. [365] in 1994 have prepared immobilized dithiocarbamate by reacting a 3 – propylethylenediamine group, covalently bonded to silica gel, with carbon disulphide in toluene. The attached dithiocarbamate possesses cation-exchange properties in which sodium ion can be exchanged with cobalt, nickel, copper and zinc from ethanolic solution. They have reported that a metal: a legand ratio of 1:3 for cobalt, 1:2 for nickel and 1:1 for copper and zinc complexes in ethanolic solution.

E. Analysis of Carbamate Pesticide Residues:

The analysis of carbamate pesticides in agriculture is now firmly established and is becoming more extensive. Thus there is a genuine need of pesticide residue analysis in our ecosystem. Several methods have been used for the detection, separation and determination of pesticides in different environmental matrices. The analysis is often complicated by chemical changes undergone by the pesticides when absorbed into living tissue, adsorbed onto the soil, or exposed to ultraviolet light or sunlight. These changes often produce compounds which are more toxic than the original pesticides and the analyst has to determine the rate of the break down, the nature and quantity of these metabolites and end – products, as well as the pesticide residue. The analysis of pesticide residues involves the following steps:

1. Detection: Preliminary characterization of pesticide residues
2. Extraction of pesticide residues
3. Clean-up or Separation
4. Pre-concentration /Enrichment
5. Determination/Estimation

1. **Detection:** Generally, a preliminary characterization of the residue is required before undertaking sophisticated and costly instrumental analysis. Spot-test analysis has been found to be inexpensive and simple for the on field detection of the residue. Different characteristics of the pesticide have been utilized to maximize the sensitivity, selectivity, and specificity of the test. Recently, several spot tests such as the capillary spot test, the thin-layer chromatographic spot test, the paper chromatographic spot test, the ion – exchange spot test and the enzymatic spot test, have been developed and used for the detection of pesticide residues at trace levels.

2. **Extraction of pesticide residues:** Several modern extraction techniques have been developed and they may be divided in the following two groups:

i. Fluid-phase partitioning method

ii. Sorptive and membrane –based extraction methods

The selection of extraction procedure to be employed is governed by the type of pesticide and nature of matrix/ sample under examination. The extraction procedure should be of improved recoveries (at least 80% efficient), higher sample throughput (sufficiently selective), less organic solvent consumption and the minimum clean-up prior to the determination.

Tadeo et al. have done a considerable piece of work in this direction. They have made multiresidue determination [366] of various herbicides and insecticides in soil. The method is based on the sonication-assisted extraction of pesticides in small columns (SAESC) using ethyl acetate and their determination and identification by capillary gas chromatography with electron-capture detector (GC-ECD) and gas chromatography with mass spectrometry (GC-MS).

In another approach they determined the pesticides [367] of various chemical classes such as organochlorines, triazines and organophosphates by GC-MS using analyte protectants to counteract the matrix (soil, juice, honey etc) effect.

3. **Clean-up or separation:** The removal of interfering substances from the extract is usually referred to as the cleanup procedure. Generally the extract must be purified or cleaned-up before the determination of the pesticide residue can be carried out. The extract normally contains co-extracted matter sufficient to interfere with the quantification. The co-extractives such as halogen impurities interfere in the electron-

capture detection, fatty materials interfere in thin- layer chromatography, and the co-extractives can affect the absorbance in spectrophotometry. The co-extractives also alter the characteristics of the chromatography column. Thus the analyst must choose an appropriate clean-up procedure. The methods such as adsorptions methods (column, planar chromatography), solvent partition, distillation and gel chromatography are generally used. The type of adsorbent and the technique used obviously depend on the nature of the co-extractive.

4. **Pre-concentration /enrichment:** Enrichment of the analyte is required in some cases before clean-up and commonly before using the sophisticated and costly end method of determination. The choice of enrichment method depends on factors such as the volatility and solubility of the pesticide residues, the degree of concentration required, and the nature of the analytical technique to be used. The following methods of preconcentration have been used:

i. **Concentration methods:** In this procedure the solvent is removed in order to enrich the dissolved residues by using the techniques such as freeze concentration, lyophilization, evaporation, distillation, reverse osmonsis, and ultrafiltration.

ii. **Isolation methods:** In this procedure the pesticide residues are taken out of solution with the help of techniques such as liquid-liquid extraction, solid –liquid extraction using activated carbons, polymeric adsorbents, in situ polymerized resins, polyurethane foam plugs, inorganic adsorbents (activated alumina, calcium phosphate, florisil, hydroxylapatite, magnesia, silica gel etc.), ion –exchange resins and precipitation.

5. **Determination/Estimation:** The methods used in the determination of residues may fall into five groups namely biological, spectrophotometric, Volumetric, chromatographic, electrochemical and radiochemical. The radiochemical methods are extremely limited in use.

i. **Bioassay:** It is based on the measurement of growth, death or some other physiological change in animals, plants or micro-organisms. Any organism which is susceptible to a pesticide may be used for the bioassay of its residues. Amongst several limitations main disadvantages are its lack of specificity and requirement of the isolation of very small quantities of toxicants from the large amount of plant or animal mass. The methods used

for bioassaying pesticide residues are dry method, wet method, diet method, and enzymatic method.

ii. **Spectroscopic and spectrophotometric methods:** These methods are simple, direct, sensitive and rapid but they do not achieve the sensitivity of thin-layer chromatography and gas chromatography. They may not be able to distinguish between the parent compound, and its metabolites and hydrolysis products but they can be used with chromatography as a confirmatory technique. Spectrophotometry is a reliable and routinely used technique that is readily available for analysts.

Sharma et al. [368] have developed a simple, rapid and sensitive fourth derivative spectrophotometric method for the determination of ziram by the formation of its golden yellow coloured copper complex after dissolving into Triton X-100 at 441nm. Beer's law is obeyed over the concentration range of 0.5-30 μg/ml at 441nm in the pH range 4-8. This method has also been used for the determination of ziram in commercial samples like zirax and ziron containing ziram and from wheat grains.

Malik et al. [369] have developed a method for the direct fourth-derivative spectrophotometric determination of fungicide ferbam (Iron(III) dimethyldithiocarbamate) in commercial samples and wheat grains by converting it into an iron (II)2,2'-bipyridyl complex which is then dissolved in Triton X-100. Beer's law is obeyed over the concentration range of 0.5-20 μg/ml in a final solution. Various parameters such as the effect of pH and interference of large number of ions in the determination of ferbam are also reported.

Rathore et al. [370] have carried out atomic absorption spectrophotometric determination of mancozeb residues, micronutrients (Mn^{2+} and Zn^{2+}) in plants. It is based on the decomposition of organic matrix by treating mancozeb with oxidizing mixture (nitric acid-perchloric acid) and the determination of zinc or manganese in the residue by using atomic absorption spectrophotometer. The lower limit of determination has been reported to be at ppm level. The results of atomic absorption spectrophotometry have been compared with those obtained by volumetry in which disodium salt of ethylenediaminetetra acetic acid, eriochrome black-T and ammonia buffer of pH 10 have been used.

iii. **Volumetric methods:** A simple, inexpensive and rapid complexometric titration [371] has been developed for the determination of mancozeb. The procedure is based on the fact that mancozeb dissolves (at ppm level) in ammonia buffer of pH 10 in presence of versenate solution. The quantification is made on the basis of versenate consumed in

the process of dissolution. The end point was detected by using visual indicator, Eriochrome Black-T, which gives wine red colour with zinc (II) and manganese (II) and changes to sky blue at the end point on titrating with versenate solution at pH 10.

Tiwari et al. [272] have developed a quick and convenient method for the milligram determination of some dithiocarbamate fungicides such as ziram, zineb, ferbam and thiram. Aliquots containing 1-5 mg of the sample is allowed to react with a calculated excess of 0.1N chloramine-T reagent in the presence of glacial acetic acid for 10 min at room temperature (27°C). When the reaction is completed, the unconsumed reagent is back titrated with 0.1N solution of sodium thiosulphate to starch end point. The results are within the error of ±1%.

iv. Chromatographic methods:

a) **High performance liquid chromatography**: This technique depends on the pesticides having sufficiently different partition coefficients in the selected solvent system. As the non-volatile pesticides are analysed by this technique an extremely wide range of pesticides can be separated.

Weissmahr et al. [373] have carried the analysis of the dithiocarbamate fungicides such as ziram, maneb and zineb and the flotation agent ethyl xanthogenate by ion-pair reversed- phase high performance liquid chromatography in the natural water. The method is based on the in situ formation of a 1:1 Cu(II)-dithioligand complex and its separation, as an ion-pair with hexane sulphonate on a C- 18 reversed-phase column and detected as 260-287 nm. Detection limit is reported to be 3 μg/l (ziram), 9μg/l (maneb) and 4 μg/l (ethyl xanthogenate).

b) **Gas chromatography:** Gas-liquid chromatography has been proved to be a largely used, most versatile and sensitive method for pesticide residue analysis.

Woodrow et al. [374] have trapped air borne particulate residues that resulted from commercial applications of the dithiocarbamate fungicides (ziram and mancozeb) on glass fiber filters at 14-16 l/min up to 24 h. Hydrochloric acid hydrolysis, with stannous chloride reduction, is used to convert these residues to carbon disulphide, which is partitioned into isooctane for assay using sulphur mode flame photometric gas chromatography. Limits of detection have been found to be about 0.3 μg (ziram) and 0.5 μg (mancozeb) per filter, which are equivalent to about 14-23 ng/m^3 (24h).

c) **Thin-layer chromatography:** It has grown rapidly in recent years and is now widely accepted as a simple, reproducible, sensitive, quick and efficient technique for the detection, separation and determination of the most pesticides.

It has been reported that the admixtures of heavy metal [375] ions such as Mn^{2+}, Fe^{3+},Co^{2+},Ni^{2+},Cu^{2+},Bi^{3+} and Ag^{+} can be separated on cellulose plates impregnated with sodium diethyldithiocarbamate using organic solvents as mobile phase.

d) Paper chromatography: This is the simple, inexpensive, rapid, sensitive and selective method of identification, estimation, detection and separation of pesticide residues. Its reproducibility is poor so it has been replaced by thin-layer chromatography.

Rathore and Kumar [376] have performed chromatography of Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Hg^{+} and Pb^{2+} on paper strips impregnated with sodium diethyl dithiocarbamate and its admixtures with SiO_2, $CaSO_4$, Na_2CO_3, NaCl, NH_4Cl, EDTA, NaOH, $CaCO_3$, Na_2HPO_4 and H_3PO_4. Several binary separations have been achieved experimentally.

e) Electrochemical techniques: The electrochemical techniques [377] such as polarography, potentiometry and voltametry were applied in the analysis of pesticide residues. The technique, electrochemical biosensors, is described in biological methods. Polarographies applied to the analysis of pesticide residues contain an oxidisable or reducible group such as nitro, halogen, carbonyl, etc. Several workers investigated the use of polarography to detect parathion, malation, bisdithiocarbamates, triphenyl tin fungicides etc. Rafiqee et al. [378] reported direct current polarographic studies of parathion in micellar medium.

f) Radiochemical techniques: The neutron activation analysis was utilized to determine elements including bromine and chlorine at traces ($1\mu g\ kg^{-1}$) in milk products and fruits. The technique is of limited use because expensive equipment and skilled technicians are involved. Radioactive isotope was used in analyzing the pesticide metabolites at the level $0.1\ \mu g\ kg^{-1}$.

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Chapter-2

Preparation and Characterization of Poly-o-toluidine Zr(IV) phosphate, Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate Cation-Exchange Materials

2.1 Introduction

The inorganic ion-exchange materials based on polyvalent metals have been established now with an excellent recognition in various disciplines, *i.e.* metal ion separation, catalysis, environmental studies, medical science (kidney dialysis), ion-selective electrodes preparation, heterogeneous solid state membranes formation and in ion-exchange fibers preparation, *etc.* Besides other advantages, these materials are important in being more stable to high temperature radiation field than the organic one [1]. Organic polymers as ion-exchangers are well known for their uniformity, chemical stability and control of their ion-exchange properties through synthetic methods [2].

In order to obtain associated organic and inorganic materials as ion-exchangers, attempts have been made to develop a new class of composite ion-exchangers by the incorporation of electrically conducting organic polymers (polyaniline, polypyrrole, polythiophene, poly-o-toluidine, poly-o-anisidine *etc.*) into the matrices of inorganic precipitates of multivalent metal acid salts. These composite materials are attractive for the purpose of creating high performance or high functional polymeric materials that are expected to provide many possibilities, termed as 'organic-inorganic' hybrid ion-exchangers [3-7] with better chemical, mechanical, and thermal stabilities, reproducibility and possessing good selectivity for heavy metals indicating its useful environmental applications. Many 'organic-inorganic' composite ion-exchangers have been developed earlier by incorporation of organic monomers into inorganic matrix, by way of pillaring or non-pillaring methods [8-18]. Few such excellent ion-exchange materials have been developed in our laboratory and successfully being used in environmental analysis [19-25].

Inorganic precipitate ion-exchanger based on organic polymeric matrix must be an interesting material, as it should possess the mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion-exchanger regarding its selectivity towards some particular metal ions [26-29]. In this regard, a number of 'organic-inorganic' composite cation-exchanger samples of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate were prepared by mixing poly-o-toluidine and Nylon-6,6 into inorganic precipitate gels of Zr(IV) phosphate, Ce(IV) phosphate and Sn(IV) phosphate under varying conditions. In order to determine the composition, size, structural and thermal properties of these materials several physico-chemical

investigations were carried out by elemental analyses, atomic absorption spectrophotometry (AAS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), spectral analyses (FTIR), thermal analyses (simultaneous TGA-DTA) and X-Ray analysis. This chapter represents the preparative conditions and physico-chemical properties of these composite cation-exchange materials.

2.2 Experimental

2.2.1 Chemicals and reagents

The main reagents used for the synthesis were:

- Zirconium oxychloride, $ZrOCl_2.8H_2O$ (99%) — CDH (India)
- Phosphoric acid, H_3PO_4 (88-93%) — Loba Chemie (India)
- Ortho-toluidine, C_7H_9N (99%) — CDH (India)
- Cerium sulphate, $Ce(SO_4)_2.4H_2O$ (99%) — Qualigens (India)
- Ammonium persulphate, $(NH_4)_2S_2O_8$ (95%) — CDH (India)
- Disodium hydrogen orthophosphate, Na_2HPO_4 — CDH (India)
- Nylon-6,6 — E-Merck (India)
- Stannic chloride, $SnCl_4.5H_2O$ (99%) — CDH (India)
- Formic acid, HCOOH (85%) — Qualigens (India)
- Hydrochloric acid, HCl (35%) — E-Merck (India)
- Nitric acid, HNO_3 — E-Merck (India)

All other reagents and chemicals were of analytical grade.

2.2.2 Instrumentation

The following instruments were used for chemical analysis and characterization of the composite materials:

- A digital pH meter – Elico (India), model LI-10; was used for measuring pH.
- UV/VIS spectrophotometer – Elico (India), model EI 301E; was used for quantitative analysis.
- Double beam atomic absorption spectrophotometer (AAS) – GBC 902 (Australia) with air-acetylene flame; was used for the quantitative determination of Pb^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}.
- A scanning electron microscope – LEO 435 VP (Australia) with attached

imaging device; was used to examine the difference in surface morphology between the parent materials and the composite.

- FTIR spectrometer – Perkin Elmer (U.S.A.), model spectrum BX; was used for recording FT–IR spectra.
- Elemental analyzer –Elementary Vario EL III, Carlo-Erba, model 1108; was used for C, H and N analyses.
- A thermal analyzer –V2.2A DuPont 9900; was used for simultaneous TGA (thermo gravimetric analysis) and DTA (differential thermal analysis) studies.
- Transmissiom electron microscope (Philips EM-400); was used for particle size determination.
- An X-ray diffractometer – Phillips (Holland), model PW 1148/89 with Cu
- Kα radiations; was used for recording powder X-ray diffraction pattern.
- An automatic temperature controlled water bath incubator shaker – Elcon (India).
- A digital muffle furnace–was used to heat the material at different temperatures.
- An air oven – Lab quip (India).
- An electronic balance (digital) – Sartorius (Japan), model 21 OS; was used for weighing purpose.
- A magnetic stirrer.
- A mortar pastel.

2.2.3 Preparation of organic-inorganic composite cation-exchange materials

2.2.3.1 Preparation of reagent solutions

0.1M solutions of Zirconium oxychloride ($ZrOCl_2.8H_2O$) and tin tetrachloride ($SnCl_4.5H_2O$) were prepared in 4M HNO_3, 0.1M $Ce(SO_4)_2.4H_2O$ prepared in 1M H_2SO_4 while ammonium persulphate solution was prepared in 2M HCl. H_3PO_4 solutions of different moralities were prepared in demineralized (DMW) water. Solutions of 20% ortho-toluidine solution of different concentration (v/v) were prepared in 2M HCl. Beads of Nylon-6,6 were dissolved in different volume of concentrated formic acid.

2.2.3.2 Preparation of polymer

2.2.3.2.1 Preparation of poly-o-toluidine

The organic polymer derivative of polyaniline that is poly-o-toluidine was prepared by mixing in similar volume ratios of the solution of 0.4M ammonium persulphate prepared in 4M HCl into 20% o-toluidine prepared in 2M HCl with continuous stirring by a magnetic stirrer for 2h at 0 °C, a green colored gel was obtained. The gel was kept for 24h at 0 °C.

2.2.3.3 Preparation of inorganic precipitate

2.2.3 3.1 Preparation of Zirconium (IV) phosphate

The method of preparation of the inorganic precipitate of Zr(IV) phosphate ion-exchanger was very similar to that of Alberti and Constantino [30], with slight modification [31] by mixing a solution of 0.1M $ZrOCl_2.8H_2O$ in 4M HCl at the flow rate at 0.5 ml min^{-1} to an aqueous solution of H_3PO_4 in different molarities. The pH of the solution was maintain at 2 and constant stirring was done during mixing using a magnetic stirrer at a room temperature (25+2 °C). The white colored gel was left for 24h at room temperature for digestion.

2.2.3.3.2 Preparation of Ce(IV) phosphate

Preparation of the inorganic precipitate of Ce(IV) phosphate ion-exchanger by mixing a solution of 0.1M $Ce(SO_4)_2.4H_2O$ prepared in 1M H_2SO_4 at the flow rate at 0.5 ml min^{-1} to a solution of H_3PO_4 in different molarities by maintaining pH of the solution. A yellowish gel type slurries were obtained that was kept 24 h at room temperature in each case.

2.2.3.3.3 Preparation of Sn(IV) phosphate

The method of preparation of the inorganic precipitate of Sn(IV) phosphate ion-exchanger was very similar to that of *Alberti Constantino* with slight modification. Stannic(IV) phosphate precipitates were obtained by adding 0.10 mol dm^{-3} stannic chloride ($SnCl_4 \cdot 5H_2O$) solution prepared in 4.0 mol dm^{-3} HCl at the flow rate of 0.50 cm^3 min^{-1} to solutions of 0.10 mol dm^{-3} disodium hydrogen orthophosphate (Na_2HPO_4) solution prepared in DMW of different molarities. The white precipitates were obtained, when the pH of the mixtures was adjusted 1.0 by adding aqueous ammonia with constant stirring.

2.2.3.4 Preparation of organic-inorganic composite cation-exchangers

2.2.3.4.1 Preparation of poly-o-toluidine Zr(IV) phosphate

The composite cation-exchanger was prepared by the sol-gel mixing of poly-o-toluidine, an organic polymer, into the inorganic precipitate of Zr(IV) phosphate. In this process, when the gels of poly-o-toluidine were added to the white inorganic precipitate of Zr(IV) phosphate with a constant stirring, the resultant mixture were turned slowly into a greenish black colored slurries. The resultant slurries were kept for 24 hours at room temperature.

Now the poly-o-toluidine based composite cation-exchanger gels were filtered off, washed thoroughly with demineralized water (DMW) to remove excess acid and any adhering traces of ammonium persulphate. The washed gels were dried over P_4O_{10} at 30 °C in an oven. The dried products were immersed in DMW to obtain small granules. Samples were converted to the H^+ form by keeping in 1M HNO_3 solution for 24 hours with occasionally shaking intermittently replacing the supernatant liquid. The excess acid was removed after several washing with DMW. The material was finally dried at 40 °C and sieving to obtain particles of particular size range (~125μm). Hence a number of poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger samples were prepared and on the basis of Na^+ ion-exchange capacity (IEC) and physical appearance, sample S-5 (Table 2.1) was selected for further studies.

Table 2.1 Conditions of preparation and the ion-exchange capacity of poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchange material

Sample No.	Mixing volume ratio					Appearance of beads after drying	Na^+ ion-exchange capacity in meq dry g^{-1}
	0.1M $ZrOCl_2.8H_2O$ in 4 M HCl	H_3PO_4 in DMW	pH of the inorganic precipitate	0.4M $(NH_4)_2S_2O_8$ in 2 M HCl	20% o-toluidine in 2M HCl		
S-1	1	1(2 M)	1	-	-	White granular	0.34
S-2	1	1(2 M)	2	-	-	White granular	1.46
S-3	-	-	-	1	1	Greenish granular	0.70
S-4	1	1(2M)	2	1	1	Greenish black	0.77
S-5	1	2(3M)	2	1	1	Greenish black	1.71
S-6	1	1.5(3M)	2	1	1	Greenish black	0.95
S-7	0.5	1(2M)	2	1	1	Greenish black	0.35
S-8	1	2.5(3M)	2	1	1	Greenish black	1.31
S-9	1	1.5(2M)	2	1	1	Greenish black	0.54
S-10	1	1.5(1M)	2	1	1	Greenish black	0.90

2.2.3.4.2 Preparation of poly-o-toluidine Ce(IV) phosphate

The composite cation-exchanger was prepared by the sol-gel mixing of poly-o-toluidine, an organic polymer, into the inorganic precipitate of Cerium(IV) phosphate. In this process, when the gels of poly-o-toluidine were added to the white inorganic precipitate of Cerium(IV) phosphate with a constant stirring, the resultant mixture were turned slowly into a greenish black colored slurries. The resultant greenish black colored slurries were kept for 24 hours at room temperature.

Hence a number of poly-o-toluidine Ce(IV) phosphate composite cation-exchanger samples were prepared and on the basis of Na^+ ion-exchange capacity (IEC) sample T-4 (Table 2.2) was selected for further studies.

Table 2.2 Conditions of preparation and the ion-exchange capacity of poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchange material

Sample No.	Mixing volume ratio					Appearance of beads after drying	Na^+ ion-exchange capacity in meq dry g^{-1}
	0.1M $Ce(SO_4)_2.4H_2O$ in 1 M H_2SO_4	H_3PO_4 in DMW	pH of the inorganic precipitate	0.4M $(NH_4)_2S_2O_8$ in 2M HCl	20% o-toluidine in 2M HCl		
T-1	1	1(2 M)	2	-	-	White granular	3.16
T-2	-	-	-	1	1	Greenish granular	0.70
T-3	1	1(2M)	2	1	1	Greenish black	0.77
T-4	0.5	3(2M)	2	1	1	Greenish black	1.04
T-5	1	1.5(3M)	2	1	1	Greenish black	0.95
T-6	0.5	1(2M)	2	1	1	Greenish black	0.75
T-7	1	1.5(1M)	2	1	1	Greenish black	0.40

2.2.3.4.3. Preparation of Nylon-6,6 Sn(IV) phosphate fibrous cation-exchange material

Stannic(IV) phosphate precipitates were obtained by adding 0.10 mol dm^{-3} stannic chloride ($SnCl_4 \cdot 5H_2O$) solution prepared in 4.0 mol dm^{-3} HCl at the flow rate of 0.50 cm^3 min^{-1} to solutions of 0.10 mol dm^{-3} disodium hydrogen orthophosphate (Na_2HPO_4) solution prepared in DMW of different molarities. The white precipitates were obtained, when the pH of the mixtures was adjusted 1.0 by adding aqueous ammonia with constant stirring. The gels of Nylon-6,6 prepared in concentrated formic acid were added into the white inorganic precipitate of Sn(IV) phosphate and mixed thoroughly with constant stirring. The white fibers were obtained which were kept for 24 h at room temperature for digestion. The supernatant liquid was decanted

and fibers were filtered by suction. The excess acid was removed by several washings with DMW and the materials were dried in an air oven over P_4O_{10} at 40 °C. The dried products were converted to H^+-form by treating with 1.0 mol dm^{-3} HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and finally dried at 50 °C. Hence, a number of samples of 'Nylon-6,6, Sn(IV) phosphate' fibrous cation-exchanger were prepared (Table 2.3) and on the basis of Na^+ ion-exchange capacity (IEC) and physical appearance of material, sample P-4 was selected for detailed studies.

Table 2.3 Conditions of preparation and the ion-exchange capacity of Nylon-6,6 Sn(IV) phosphate composite cation-exchange material

Sample No.	Mixing volume ratio					Appearance of fiber after drying	Na^+ ion-exchange capacity in (m mol g^{-1})
	0.1 mol dm^{-3} $SnCl_4.5H_2O$ in 4 mol dm^{-3} HCl	0.1 mol dm^{-3} Na_2HPO_4 in DMW	pH of the inorganic precipitate	Nylon-6,6 (gm)	Formic acid (ml)		
P-1	2	2	1	-	-	White granular	2.35
P-2	0.5	1.5	1	1	10	White fiber	1.47
P-3	1.5	1.5	1	2	10	White fiber	1.88
P-4	2	2	1	1	10	White fiber	2.1

2.2.4.1 Heat treatment

To study the effect of drying temperature, 1 g samples of the composite cation-exchanger material (S-5, T-4 and P-4) were heated at different temperatures in a muffle furnace for 1 hour each; physical appearance and the percentage of weight loss were determined after cooling them at room temperature as shown in Table 2.4, 2.5 and 2.6.

Table 2.4 Thermal stability of poly-o-toluidine Zr(IV) phosphate (S-5) after heating to various temperatures for 1 h

Heating temperature (°C)	Appearance (Color)	Weight loss (%)	Na^+ Ion-exchange capacity (meq dry gm^{-1})	% Retention of IEC
50	Black	-	1.71	100
100	Black	4.00	1.71	100
150	Black	8.00	1.71	100
200	Black	16.00	0.86	50.53
300	Black	27.20	0.83	48.77
400	Black	35.20	0.76	44.56
450	Light gray	47.40	0.86	50.53
500	Light gray	63.60	0.89	51.75
600	Light gray	68.20	0.37	21.75
650	Light gray	68.08	0.35	20.94
700	Light gray	69.40	0.32	18.54

Table 2.5 Thermal stability of poly-o-toluidine Ce(IV) phosphate (T-4) after heating to various temperatures for 1h

Heating temperature (°C)	Appearance (Color)	Weight loss (%)	Na^+ Ion-exchange capacity (meq dry gm^{-1})	% Retention of IEC
50	Black	-	1.04	100
100	Black	2.00	1.04	100
150	Black	8.00	0.95	91.35
200	Black	16.00	0.84	80.77
300	Black	27.20	0.80	76.92
400	Black	32.20	0.72	69.23
450	Light gray	47.40	0.86	82.69
500	Light gray	50.60	0.65	62.50
600	Light gray	58.20	0.42	40.38
650	Light gray	58.08	0.35	33.46

Table 2.6 Thermal stability of Nylon-6,6 Sn(IV) phosphate (P-4) after heating to various temperatures for 1 h

Heating temperature (°C)	Appearance (Color)	Weight loss (%)	Na^+ Ion-exchange capacity (m mol gm^{-1})	% Retention of IEC
50	White fiber	-	2.10	100
100	White fiber	-	2.10	100
150	Light brown	4.00	1.70	80.95
200	Light brown	6.50	1.46	69.52
300	Light brown	11.0	1.23	58.57
400	Light brown	18.7	0.95	45.24

2.2.4.2 Chemical composition

The chemical composition plays an important role in the elucidation of molecular structure of the ion-exchangers. The composition of the material can be determined either by gravimetrically or spectrophotometrically. With the help of these methods, we can determine the percentage of metals or groups present in the ion-exchangers.

To determine chemical composition of poly-o-toluidine Zr(IV) phosphate (Sample S-5, original form), poly-o-toluidine Ce(IV) phosphate (Sample T-4, original form) and Nylon-6,6 Sn(IV) phosphate (Sample P-4, original form), two hundred mg of the each cation-exchanger were dissolved in 20 ml of concentrated H_2SO_4. The materials were analyzed for 'zirconium(IV)', 'cerium (IV)' and 'tin(IV)' by ICP-MS and phosphorus by the phosphovanado molybdate method. Carbon, hydrogen and nitrogen content of the cation-exchanger were determined by elemental analysis. The weight percent composition of POTZr(IV)P, POTCe(IV)P, NYSn(IV)P are given in Table 2.7.

Table 2.7 Percent composition of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchangers

S. No.	Poly-o-toluidine Zr(IV) phosphate		Poly-o-toluidine Ce(IV) phosphate		Nylon-6,6 Sn(IV) phosphate	
	Elements	Percentage	Elements	Percentage	Elements	Percentage
1	C	38.75	C	57.89	C	57.34
2	H	4.478	H	5.848	H	9.76
3	O	10.034	O	10.26	O	23.13
4	N	7.938	N	11.79	N	10.73
5	Zr	26.3	Ce	6.452	Sn	8.09
6	P	12.5	P	7.79	P	0.95

2.2.4.3 Determination of phosphorous

2.2.4.3.1 Preparation of reagent solutions

a) Ammonium vanadate solution: 2.5 g of ammonium vanadate (NH_4VO_3) was dissolved in 500 ml hot water, followed by the addition of 20 ml concentrated nitric acid and diluted with water to 1 L in a graduated flask.

b) Ammonium molybdate solution: 50 g of ammonium molybdate [$(NH_4)_6Mo_7O_{34}.4H_2O$] was dissolved in warm water and diluted to 1 L in a graduated flask, the solution was used after filtration.

2.2.4.3.2 Procedure

Ten milliliter of the supernant liquid was taken in a 25 ml volumetric flask, and 2 ml of (2:1) (nitric acid: DMW) solution followed by the addition of 2 ml of ammonium vanadate solution, and 2 ml of the ammonium molybdate solution were added and diluted to the mark through mixing. The absorbance was recorded at 465 nm against a blank solution prepared in the same manner, using 1cm cell. A series of standard solution of di-sodium hydrogen orthophosphate covering the range, 100-1000 ppm phosphorous per 100 ml were prepared containing the same concentration of acid, ammonium vanadate and ammonium molybdate as the previous solution. The amount of phosphorus was determined by using a standard curve drawn as per the same procedure by taking known amount of phosphorous.

2.2.4.4 Transmission electron microscopy (TEM) studies

Fine particle dispersion method was used for sample preparation in which sample materials poly-o-toluidine Zr(IV) phosphate (S-5), poly-o-toluidine Ce(IV) phosphate (T-4) and Nylon-6,6 Sn(IV) phosphate (P-4) were grind in mortar pastel to obtain fine particles. The fine particles are dispersed in a volatile liquid (alcohol) by stirring which separates the agglomerated particles and ensures a homogenous suspension. A dilution step is often required to obtain very low concentrations of the material, so that the particles on the support film remain isolated. A droplet of the sample suspension is placed on the copper coated grid. The specimen is ready for observation after complete evaporation or drying. Transmission electron microscopy was performed in a CM 200 Phillips microscope with an acceleration voltage of 200 kV to know the particle size of the poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchange materials.

2.2.4.5 Scanning electron microscopy (SEM) studies

Microphotographs of the original form of poly-o-toluidine (sample S-3); Zr(IV) phosphate (sample S-2) and poly-o-toluidine Zr(IV) phosphate (sample S-5); poly-o-toluidine (sample T-2), Ce(IV) phosphate (sample T-1) and poly-o-toluidine Ce(IV) phosphate (sample T-4); Sn(IV) phosphate (sample P-1) and Nylon-6,6 Sn(IV) phosphate (sample P-4) were obtained by the scanning electron microscope at various magnifications. The sample in finely powdered form placed on studs with the help of adhesive tape. There is no need of coating the sample, as the sample is a conducting composite. After putting the stud in SEM machine, images appear when beam get scattered from the sample.

2.2.4.6 X- ray studies

Powder X-ray diffraction (XRD) pattern was obtained in an aluminum sample holder for the sample S-5 (poly-o-toluidine Zr(IV) phosphate), sample T-4 (poly-o-toluidine Ce(IV) phosphate) and sample P-4 (Nylon-6,6 Sn(IV) phosphate) in the original form using a PW 1148/89 based diffractometer with Cu Kα radiations.

2.2.4.7 Fourier transform infrared (FTIR) spectroscopic studies

The FTIR spectrum of poly-o-toluidine (sample S-3), Zr(IV) phosphate (sample S-2)

and poly-o-toluidine Zr(IV) phosphate (sample S-5); poly-o-toluidine (sample T-2), Ce(IV) phosphate (sample T-1) and poly-o-toluidine Ce(IV) phosphate (sample T-4); Sn(IV) phosphate (sample P-1) and Nylon-6,6 Sn(IV) phosphate (sample P-4) in the original form dried at 40 °C were taken by KBr disc method at room temperature.

2.2.4.8 Thermogravimetric analysis-differential thermal analysis (TGA-DTA) studies

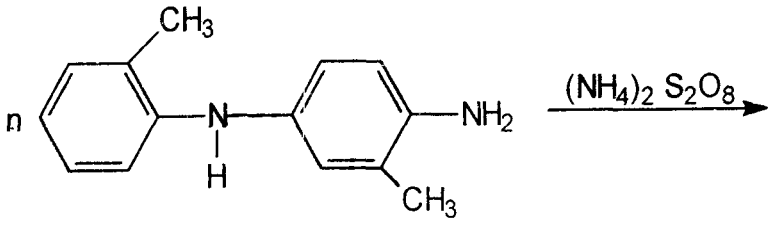
Simultaneous TGA and DTA studies of the composite cation-exchange materials (poly-o-toluidine Zr(IV) phosphate, S-5; poly-o-toluidine Ce(IV) phosphate, T-4 and Nylon-6,6 Sn(IV) phosphate, P-4) in original form were carried out by an automatic thermo balance on heating the material from 10 °C to 1000 °C at a constant rate (10 °C per minute) in the air atmosphere (air flow rate of 400 ml min^{-1}).

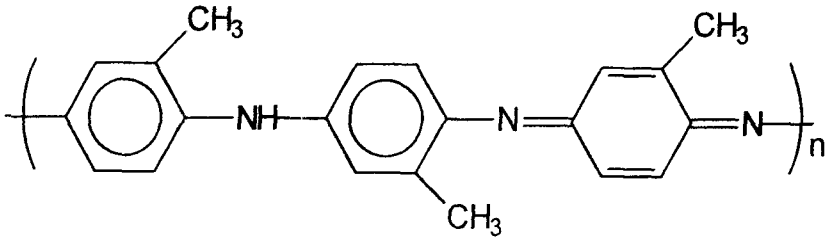
2. 3 Results and Discussion

2.3.1 Preparation of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate nano-composites and Nylon-6,6 Sn(IV) phosphate fibrous cation-exchangers

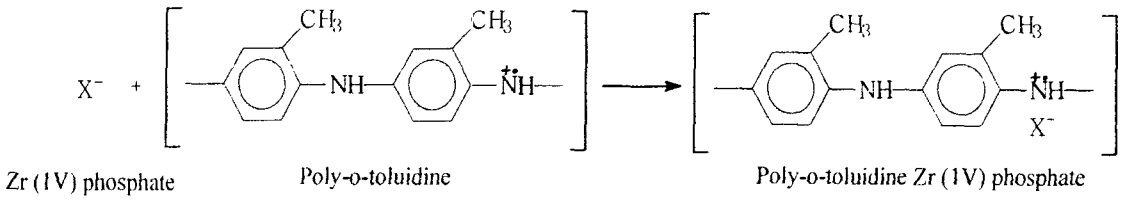
Poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite ion exchange materials were prepared by incorporation poly-o-toluidine and Nylon-6,6 solution into inorganic matrices of Zr(IV) phosphate, Ce(IV) phosphate and Sn(IV) phosphate, respectively by changing the mixing volume ratios. Among them, sample S-5 (Table 2.1) possed better Na^+ ion-exchange capacity (1.71 meq dry g^{-1}) as compared to Zr(IV) phosphate (1.46 meq dry g^{-1}); sample T-4 (Table 2.2) with Na^+ ion-exchange capacity (1.04 meq dry g^{-1}) as compared to Ce(IV) phosphate (3.16 meq dry g^{-1}) and sample P-4 (Table 2.3) with better Na^+ ion-exchange capacity (2.1 meq dry g^{-1}) as compared to Sn(IV) phosphate (1.12 meq dry g^{-1}), good yield and thermal stabilities were selected.

The polymerization reaction for the synthesis of poly-o-toluidine is given as follows.

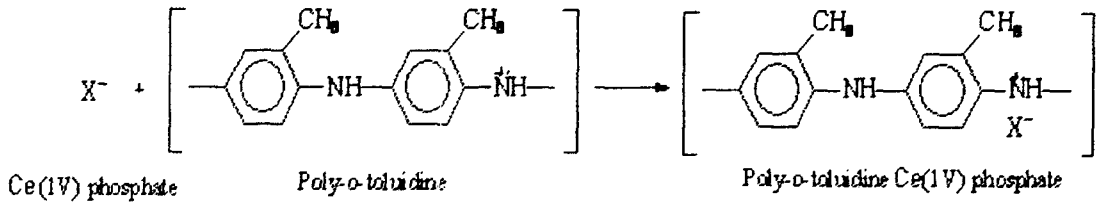




The binding of poly-o-toluidine into the matrix of Zr(IV) phosphate (assumed as X in the reaction) can be as:



The binding of poly-o-toluidine into the matrix of Ce(IV) phosphate (assumed as X in the reaction) can be as:



A fibrous composite Nylon-6,6 Sn(IV) phosphate was prepared by mixing inorganic precipitate of Sn(IV) phosphate and Nylon-6,6 developed in formic acid in different (w/v) ratio's. The maximum ion-exchange capacity of the composite was found to be 2.1 meq/g for Na^+ ions.

2.3.2 Thermal stability

On heating at different temperature for 1 hour, the mass and physical appearance of the dried sample materials (S-5, T-4 and P-4) were changed as the temperature increased as shown in Tables 2.4, 2.5 and 2.6. The materials were found to possess higher thermal stability as the sample S-5 (poly-o-toluidine Zr(IV) phosphate)

maintained about 31.8% of the initial mass by heating upto 600 °C; sample T-4 (poly-o-toluidine Ce(IV) phosphate) maintained about 42% of the initial mass by heating upto 600 °C and sample P-4 (Nylon-6,6 Sn(IV) phosphate) maintained about 31% of the initial mass by heating upto 400 °C.

2.3.3 TEM (Transmission Electron Microscopy) studies

From the TEM studies it is clear that the poly-o-toluidine Zr(IV) phosphate shows particles size in range of 42.0 to 100.0 nm (Figure 2.1) while poly-o-toluidine Ce(IV) phosphate having partical size 31.0 to 43.23 nm (Figure 2.2).Thus the material particle size show the nano-range.

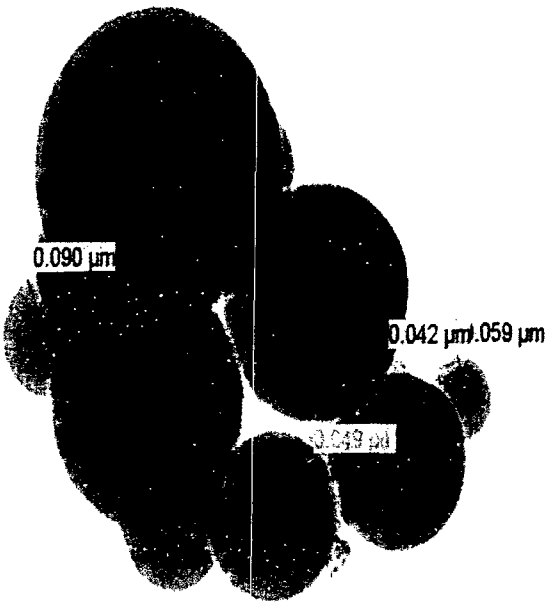


Figure 2.1 Transmission electron microphotographs (TEM) of poly-o-toluidine Zr(IV) phosphate showing different particle size

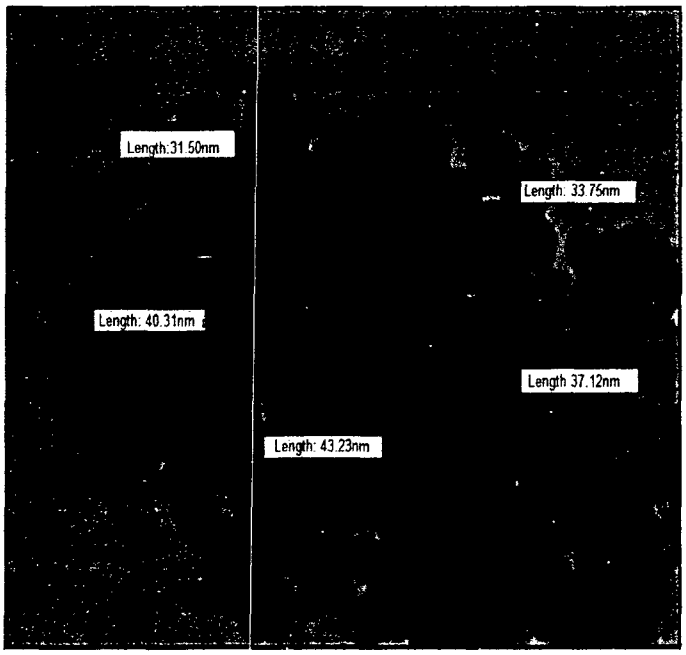


Figure 2.2 Transmission electron microphotographs (TEM) of poly-o-toluidine Ce(IV) phosphate showing different particle size

2.3.4 SEM (Scanning Electron Microscopy) studies

Scanning electron microscopy (SEM) studies were performed to examine the difference in surface morphology between the parent materials and their composites. SEM photographs of poly-o-toluidine, Zr(IV) phosphate and poly-o-toluidine Zr(IV) phosphate; poly-o-toluidine Ce(IV) phosphate and poly-o-toluidine Ce(IV) phosphate; and Sn(IV) phosphate and Nylon-6,6 Sn(IV) phosphate were obtained at different magnifications (Figure 2.3, Figure 2.4 and Figure 2.5), indicating the binding of inorganic ion-exchange materials to organic polymers. The SEM pictures of the composites show the difference in surface morphology of organic polymers, inorganic precipitates and composite materials.

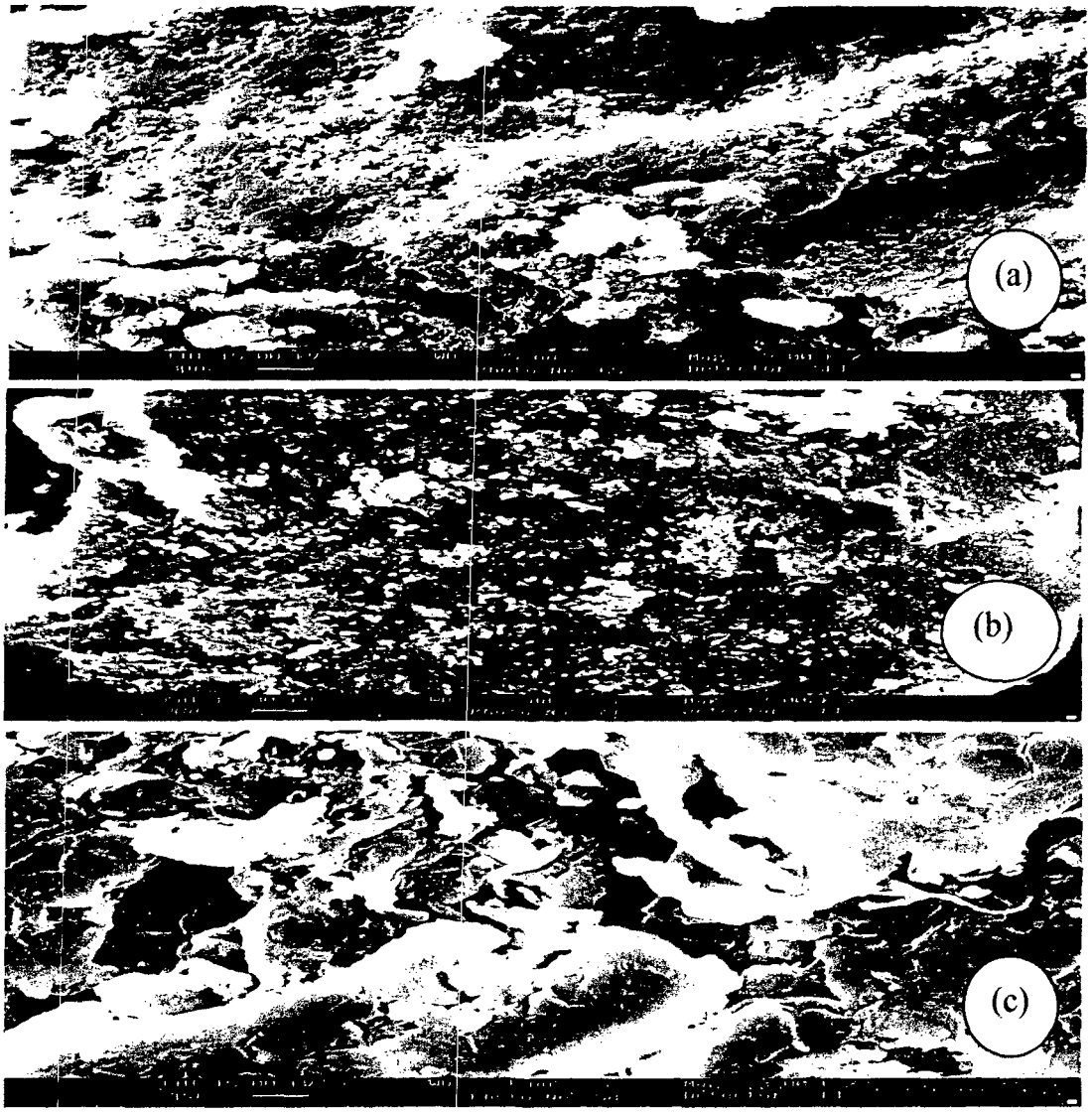


Figure 2.3 Scanning electron microphotographs (SEM) of chemically prepared (a) poly-o-toluidine at the magnification of 2000 × , (b) Zr(IV) phosphate at the magnification of 2000 × and (c) poly-o-toluidine Zr(IV) phosphate composite system at the magnification of 3000 ×

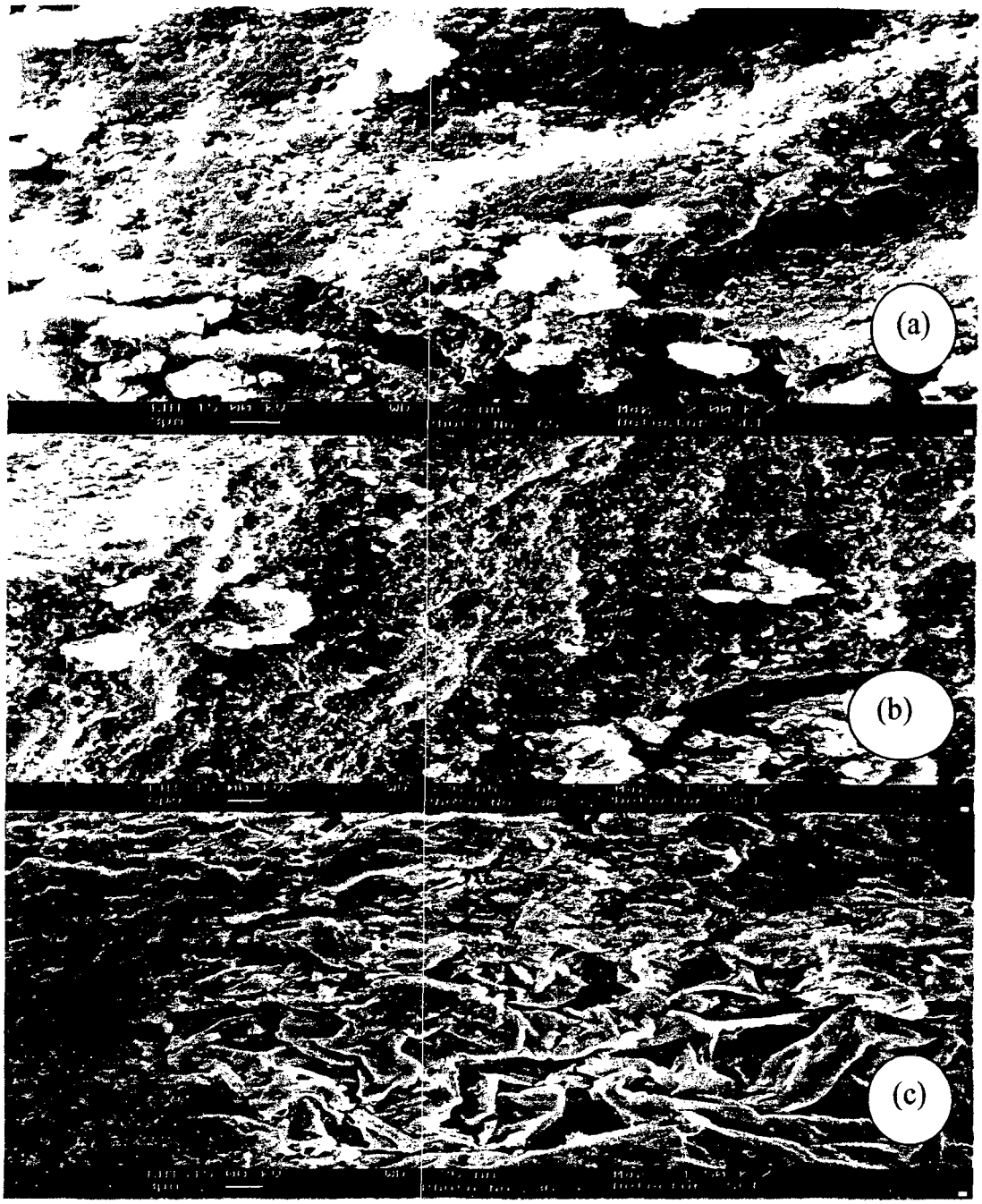


Figure 2.4 Scanning electron microphotographs (SEM) of chemically prepared (a) poly-o-toluidine at the magnification of 2000 × , (b) Ce(IV) phosphate at the magnification of 1500 × and (c) poly-o-toluidine Ce(IV) phosphate composite system at the magnification of 1500 ×

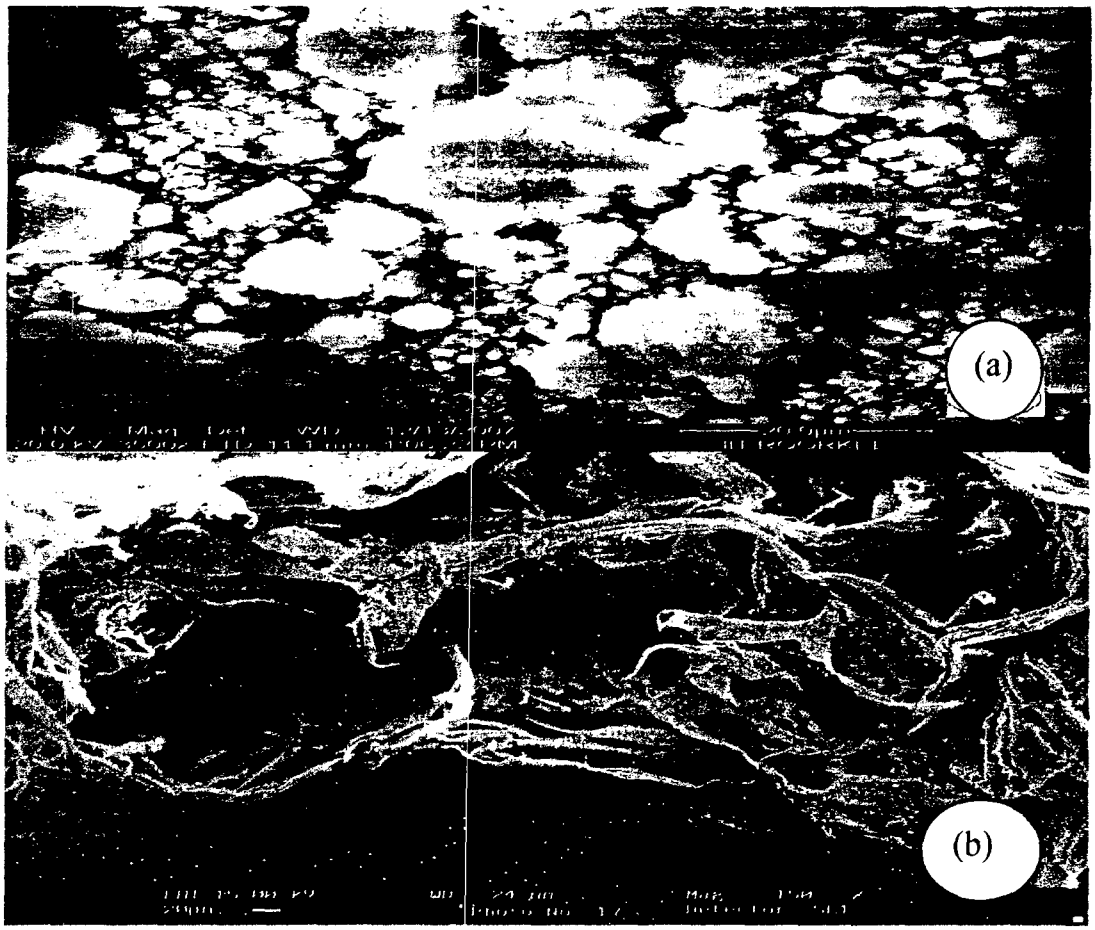


Figure 2.5 Scanning electron microphotographs (SEM) of chemically prepared (a) Sn(IV) phosphate at the magnification of 3500 × and (b) Nylon-6,6 Sn(IV) phosphate composite system at the magnification of 1500 ×

2.3.5 X- ray studies

The X-ray diffraction pattern of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate (S-5, T-4 and P-4, as prepared) showed very small peaks. The analysis of these small signal supports towards its semi-crystalline nature (Figure 2.6a, Figure 2.6b and Figure 2.6c).

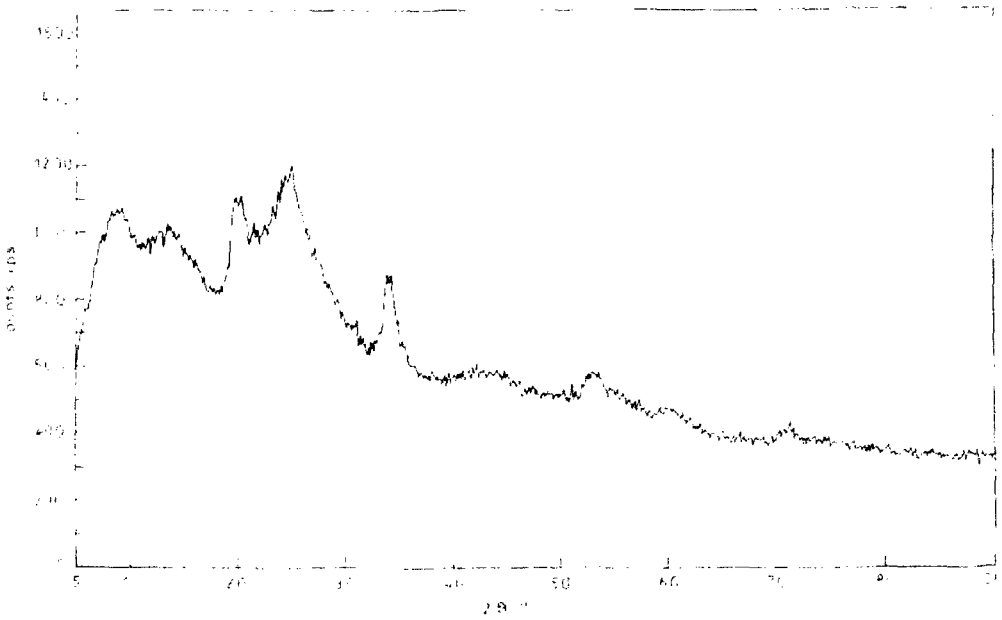


Figure 2.6a Powder X-ray diffraction pattern of poly-o-toluidine Zr(IV) phosphate composite (as prepared)

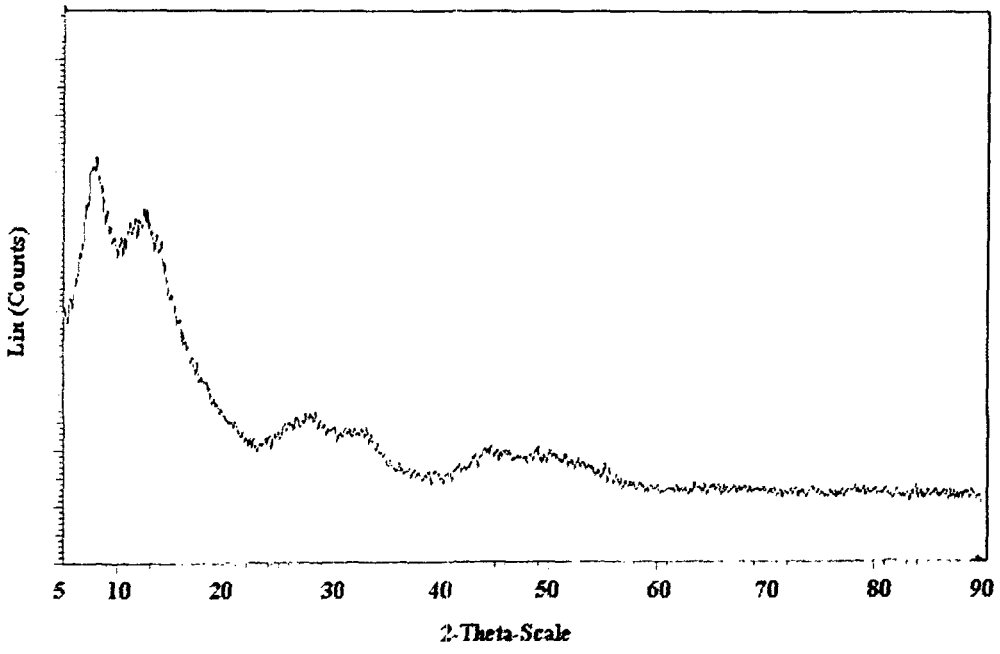


Figure 2.6b Power X-ray diffraction pattern of poly-o-toluidine Ce(1V) phosphate composite (as prepared)

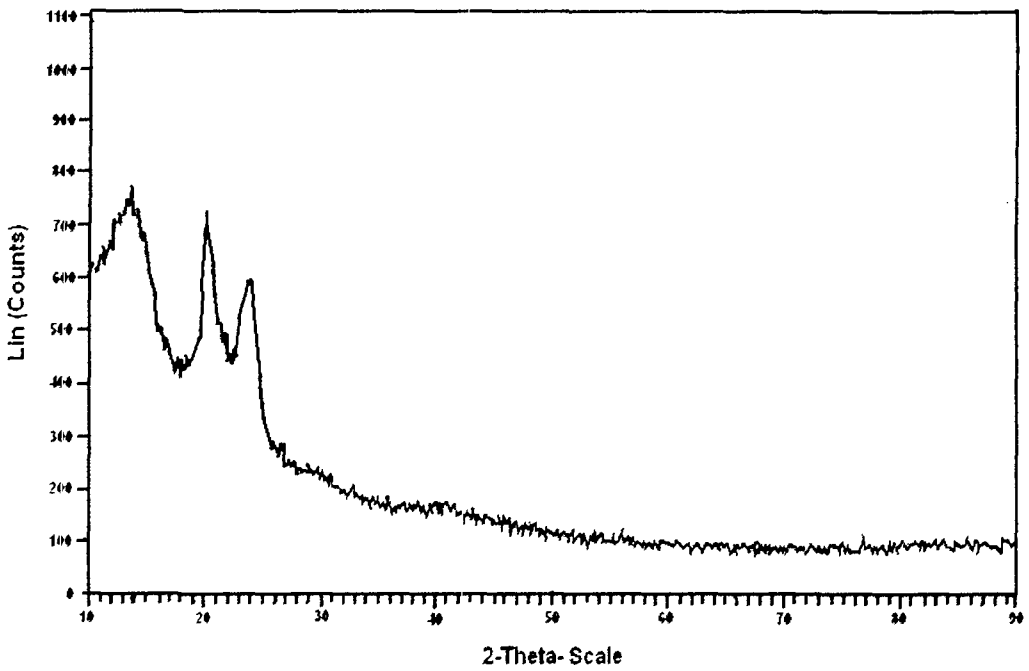


Figure2.6c Powder X-ray diffraction pattern of Nylon-6,6 Sn(IV) phosphate fibrous composite (as prepared)

2.3.6 FTIR studies

The FT-IR spectra of poly-o-toluidine, Zr(IV) phosphate and poly-o-toluidine Zr(IV) phosphate are shown in Figure 2.7. The FTIR spectrum of the composite cation-exchanger, sample S-5 (Figure 2.7c) showed that the presence of extra water molecule in addition to the – OH groups and metal oxides present internally in the material. In the spectrum a strong broad band around 3400 cm^{-1} found which could be attributed to – OH stretching frequency. The peak at the around 1600 cm^{-1} may be due to interstitial water present in the composite material [32]. An assembly of three peaks in the 500-800 cm^{-1} region showed the presence of ionic phosphate groups [33] as well as metal oxygen bonds present in the material. The additional band at around 1400 cm^{-1} can be ascribed to stretching vibration of C-N [34]. This indicates that the material contains considerable amount of poly-o-toluidine. These vibration frequencies are in close resemblance with the FTIR spectrums of poly-o-toluidine (Figure 2.7a) and poly-o-toluidine Zr(IV) phosphate (Figure 2.7c).

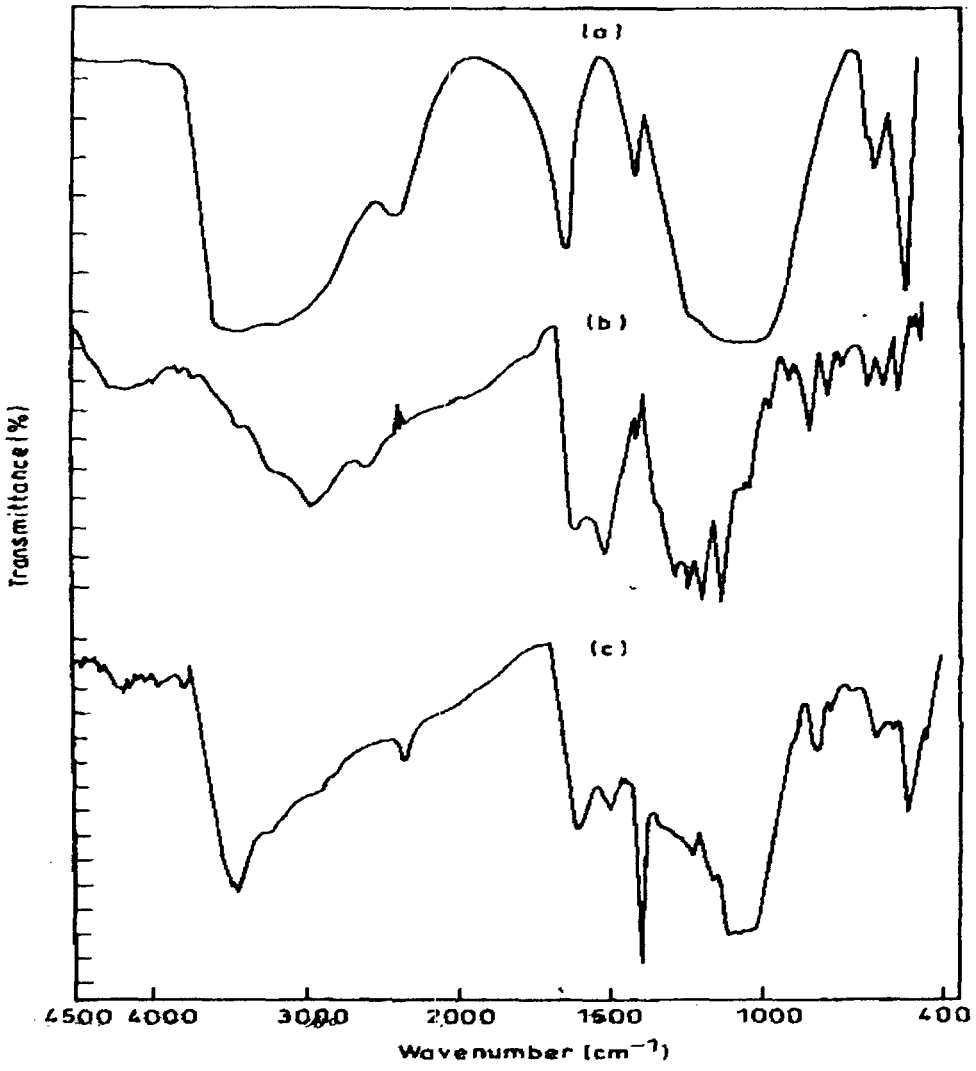


Figure 2.7 FTIR spectra of as prepared poly-o-toluidine (a), Zr(IV) phosphate (b) and poly-o-toluidine Zr(IV) phosphate composite material (c)

The FTIR spectra of poly-o-toluidine, Ce(IV) phosphate and poly-o-toluidine Ce(IV) phosphate are shown in Figure 2.8. The FTIR spectrum of the composite cation-exchanger, sample S-4 showed that the presence of extra water molecule in addition to the – OH groups and metal oxides present internally in the material. A sharp peak around 1600 cm^{-1} can be attributed to H–O–H bending band, which represents the strongly bonded –OH groups in the matrix [35]. An assembly of broad peaks in the region 500–800 cm^{-1} may be due to the presence of aqua waging twisting and rocking modes of metal oxygen bond [32,36], while a sharp peak at about 1200 cm^{-1}may be due to the superposition of metal oxygen stretching vibrations [υ_2 Ce–O] [37]. Absorption in the range about 1450–1600 cm^{-1} referred to

stretching of C–N bonds of benzenic and quinonic rings. Another assembly of three bands in the region 1300–1600 cm^{-1} may be ascribed to the stretching vibration frequency of C–N bonds [34] and a band around 3000 cm^{-1} may be related to the stretching of NH bonds of benzenic and quinonic rings [38] present in the material (Figure 2.8 (c)). Further these vibration frequencies in Figure 2.8 (c) resemble the stretching vibration frequencies for C–N and NH bonds found in poly-o-toluidine (Figure 2.8(a)).

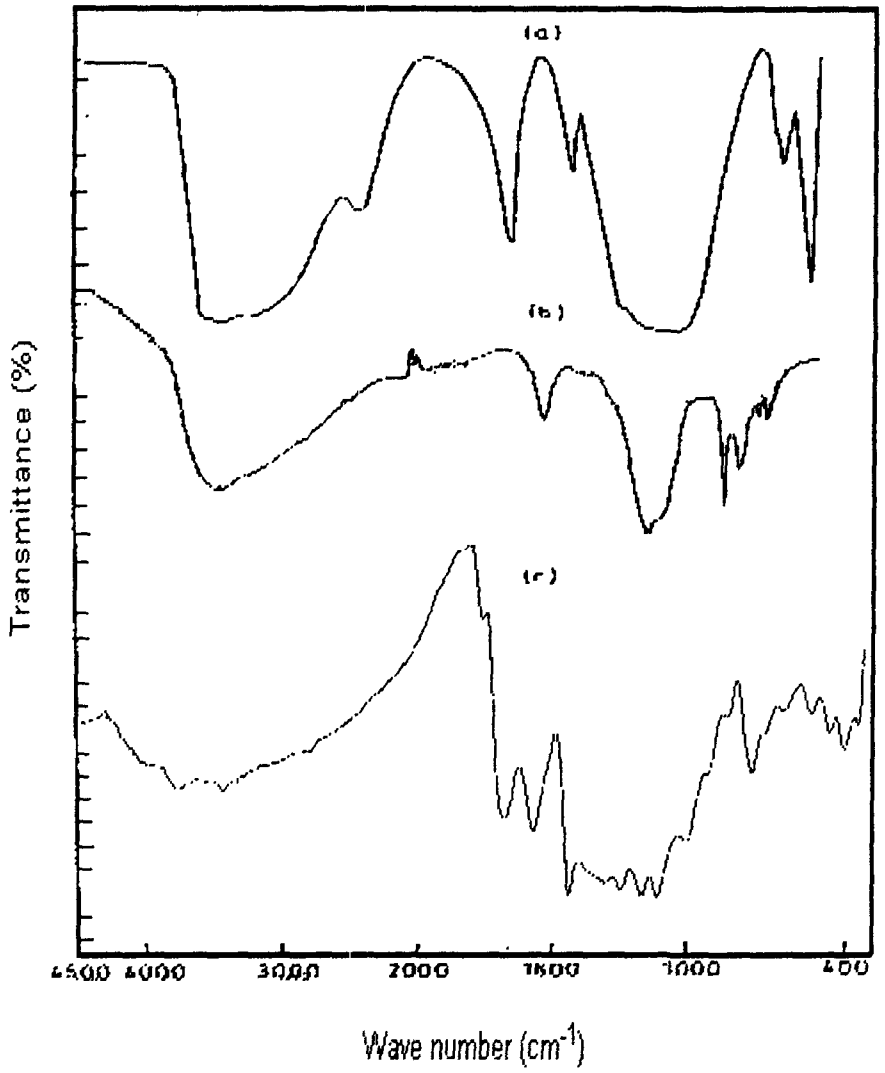


Figure 2.8 FTIR spectra of as prepared poly-o-toluidine (a), Ce(IV) phosphate (b) and poly-o-toluidine Ce(IV) phosphate composite material (c)

Figure 2.9 shows FTIR spectra of as-prepared Sn(IV) phosphate and Nylon-6,6 Sn(IV) phosphate fibrous cation-exchange materials. The FTIR spectrum of cation-exchange material Nylon-6,6 Sn(IV) phosphate (Figure 2.9b) revealed the

presence of the external water molecules in addition to the metal-oxygen and metal - OH stretching band. In the spectrum a broad band in the region at 3434 cm^{-1} may be due to the presence of external water molecules. While a sharp peak in region 1638 cm^{-1} is the indication of the presence of water of crystallization. A less broad peak around in the region 1027 cm^{-1} may be due to the presence of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{2-}$ [39]. This fibrous cation-exchanger also showed a strong band at 1638 cm^{-1} corresponding to the carbonyl group of Nylon-6,6 and a small peak in the region 1465 cm^{-1} as a band of medium intensity mainly due to the C-H bending of methylene groups of Nylon-6,6 moiety [40]. The absorption band in the region 1542 cm^{-1} may be due to the N-H stretching frequency of amide group of Nylon-6,6 [41]. An assembly of small peaks in the region 500–950 cm^{-1} is due to the superposition of metal-oxygen stretching vibrations. These characteristic stretching frequencies are also in close resemblance with the inorganic precipitate, i.e. Sn(IV) phosphate (Figure 2.9a) and Nylon-6,6 Sn(IV) phosphate (Figure 2.9b), indicating the binding of inorganic precipitate with organic polymer and formation of 'polymeric–inorganic' fibrous Nylon-6,6 Sn(IV) phosphate.

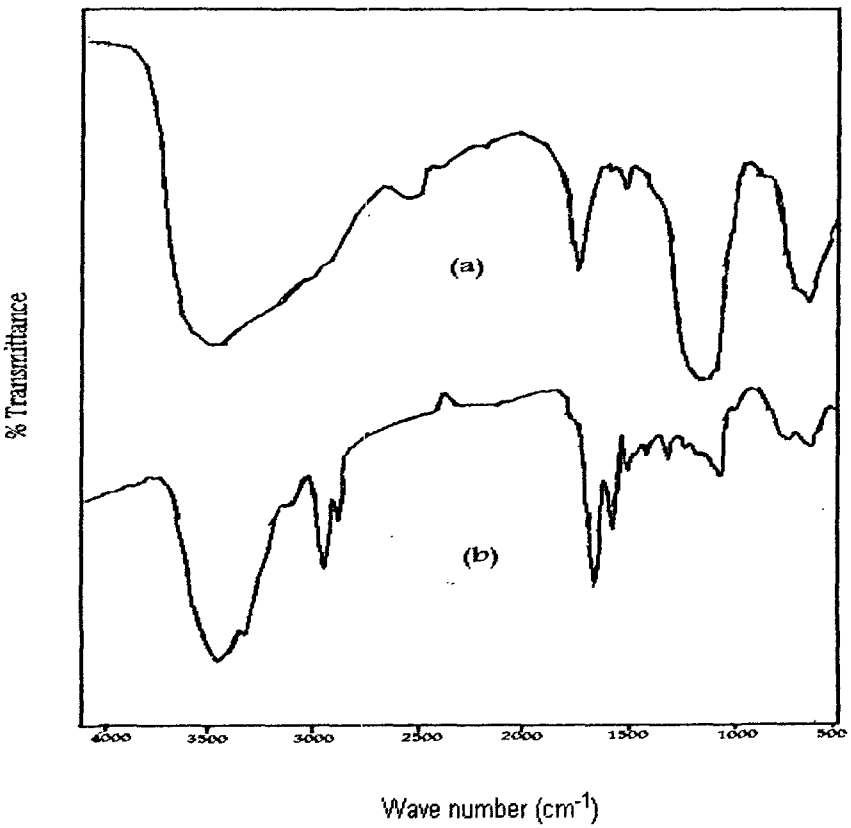


Figure 2.9 FTIR spectra of as prepared Sn(IV) phosphate (a) and Nylon-6,6 Sn(IV) phosphate fibrous composite material (b)

2.3.7 TGA-DTA (Thermogravemetric Analysis-Differential Thermal Analysis) studies

The thermogravimetric analyses (TGA-DTA) curve (Figure 2.10) of poly-o-toluidine Zr(IV) phosphate material showed continuous weight loss of mass (about 10%) up to 150 °C, which may due to removal of external water molecule [42]. Further weight loss of mass in between 149-350 °C may be due to the condensation of intramolecular hydroxyl group. A steep weight loss of mass observed in the temperature range 350-500 °C may be due to the conversion of phosphate group to pyrophosphate. Slight decomposition of organic part may be observed in the temperature range 500-650 °C. At 650 °C onwards, a smooth horizontal section represented the complete formation of the oxide form of the material. The DTA curve shows the reaction is exothermic during the change of phase of material, broad peaks at 280 °C and at 480 °C can be observed.

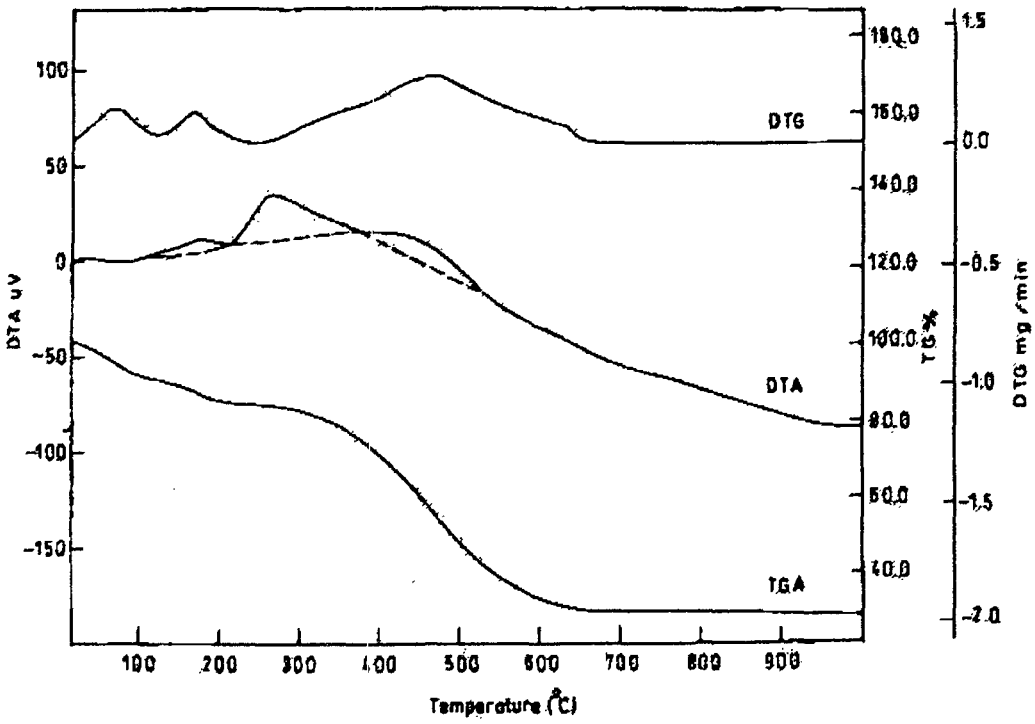


Figure 2.10 Simultaneous TGA-DTA curves of poly-o-toluidine Zr(IV) phosphate (as prepared)

It is clear from the thermogravimetric analysis (TGA) curve (Figure 2.11) of poly-o-toluidine Ce(IV) phosphate material that upto 100 °C only 2 % weight loss was observed, which may be due to the removal of external H_2O molecules present at the surface of the composite [42]. Further weight loss of mass approximately ~20% between 100 to 200 °C may be due to the slight conversion of inorganic phosphate into pyrophosphate. Slow weight loss of mass about ~25% in between 200-600 °C may be due to the slight decomposition of organic part of the material. A broad peak at 500 °C in DTA curve shows the reaction is exothermic during the change of phase of material.

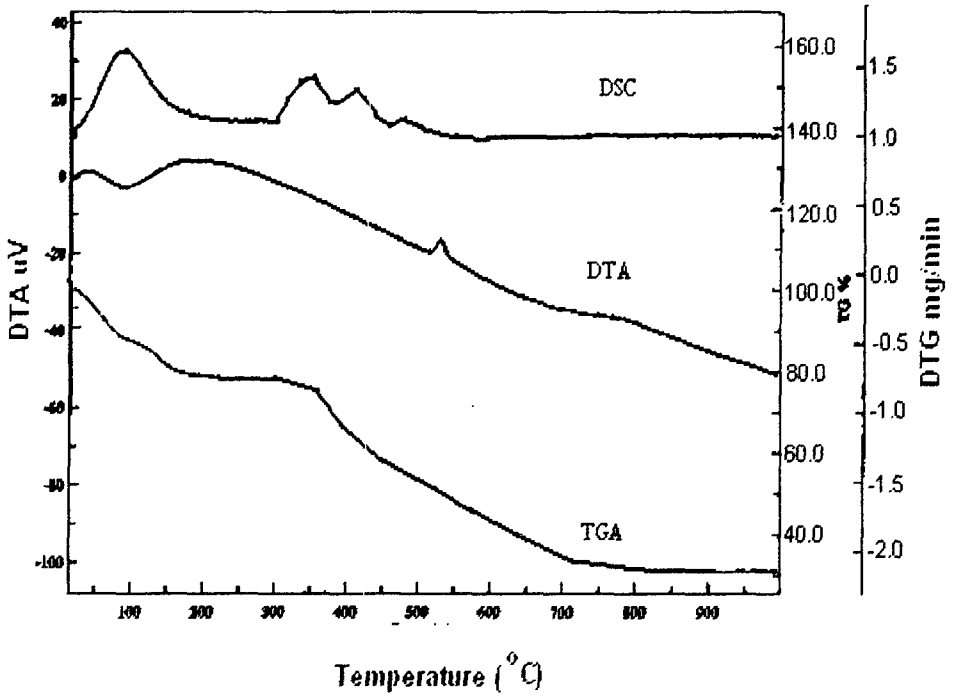


Figure 2.11 Simultaneous TGA-DTA curves of poly-o-toluidine Ce(IV) phosphate (as prepared)

As evident from the thermogravimetric analysis curve (Figure 2.12) of Nylon-6,6 Sn(IV) phosphate fibrous cation-exchanger initial weight loss of mass ~11% up to 200 °C may be due to the loss of external water molecule present [42]. Slow weight loss observed between 200 °C to 350 °C may be due to the condensation of phosphate group to pyrophosphate groups. Further weight loss between 350 °C to 450 °C may be due to complete decomposition of the organic part of the material. At 450 °C onwards, a smooth horizontal section which represents the complete formation of

the oxide form of the material. A broad peak at ~500 °C in DTA curve shows the reaction is exothermic during the change of phase of the material.

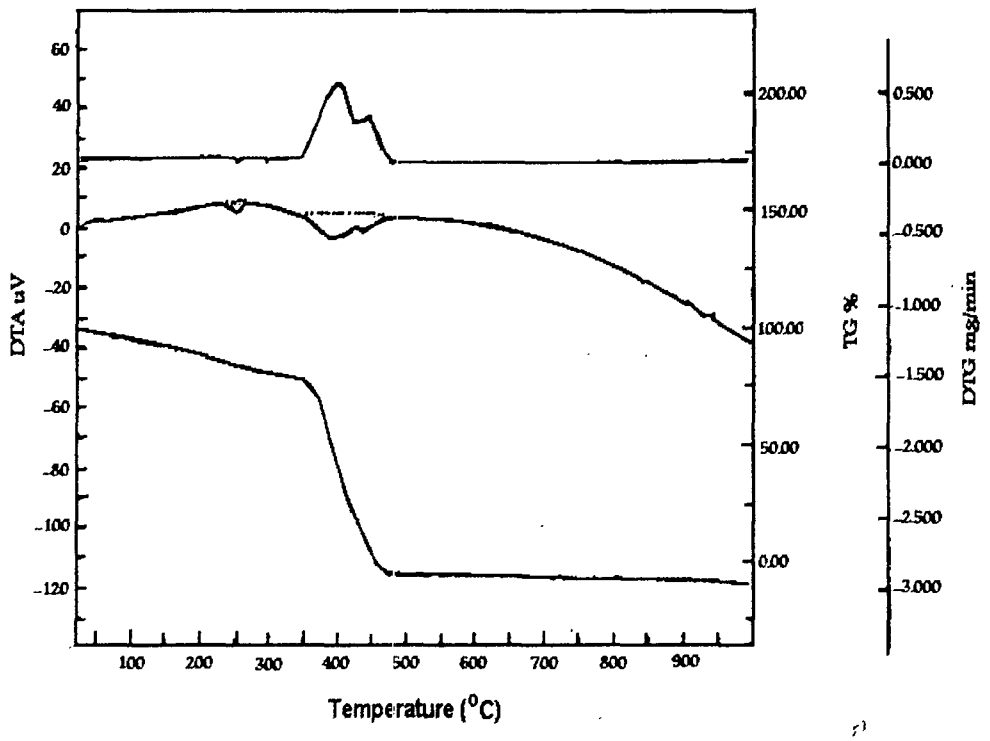
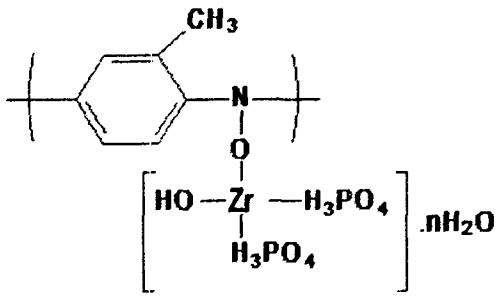


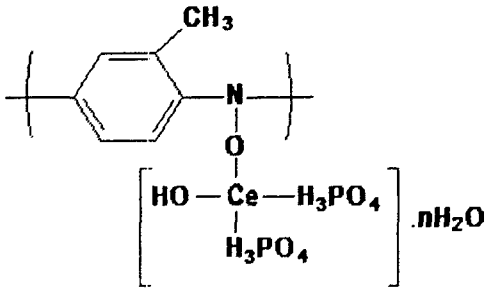
Figure 2.12 Simultaneous TGA-DTA curves of Nylon-6,6 Sn(IV) phosphate (as prepared)

2.3.8 Chemical composition and chemical structure

The percent composition of Zr, P, C, H, N, and O in Poly-o-toluidine Zr(IV) phosphate was found to be 26.3, 12.5, 38.75, 4.478, 7.938 and 10.034. (Table 2.7). On the basis of elemental analysis tentative structure of the nano-composite cation exchanger is given as follows:



The percent composition of C, H, O, N, P and Ce for Poly-o-toluidine Ce(IV) phosphate were analyzed as: 57.89, 5.848, 10.26, 11.79, 7.76 and 6.452. (Table 2.7) which can suggest the following tentative formula of the material:



The percent composition of Sn, P, C, H, N and O for Nylon-6,6 Sn(IV) phosphate was found to be 8.09, 0.95, 57.34, 9.76, 10.73, 23.13. A tentative structure can be proposed;

$$[Sn(HPO_4)_2 \cdot (-CO- (CH_2)_4- CO-NH- (CH_2)_6- N-)] \cdot nH_2O$$

References

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Chapter-3

Ion-Exchange Properties of Poly-o-toluidine Zr(IV) phosphate, Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate Cation-Exchange Materials

3.1 Introduction

Synthetic inorganic ion-exchangers have been established [1-3] their place in analytical chemistry due to their resistant to heat, radiation and their differential selectivity for metal ions. A large number of such materials have been synthesized earlier, most of which are the hydrous oxides and the hetero poly-acids salts of the tetra and pentavalent metals. These compounds have shown great promise in analytical chemistry because of their separation potential of metals [4]. Every synthetic inorganic ion-exchanger has specific selectivity towards one or two metallic species. They are also highly stable to a wide range of pH and upto high temperature. However, their real analytical applications in various fields are still lacking.

Two component inorganic ion-exchangers have much studied as compared to three component ion-exchangers. The compound containing two different cations and one anion or two different anions and one cation (*i.e.* three component ion-exchangers) show specific selectivity and higher thermal stability. A number of two component [5, 6] and three component [7,8] ion-exchangers have been established for the selective determination of heavy toxic metal ions. Since organic polymers as ion-exchangers, are well known for their uniformity, chemical stability and control of their ion-exchange properties through synthetic methods [9-12]. Derivatization of inorganic ion-exchangers by organic molecules depends on the nature of the inorganic matrix. Tetravalent metal acid salts can be derivatized by organic moieties bearing inorganic groups such as -OH, -COOH, $-SO_3H$, $-NH_2$, -NH *etc.* which also act as ion-exchangers, and are known as 'organic-inorganic' ion-exchangers [13-23].

'Organic-inorganic' composite ion-exchangers with better mechanical and granulometric properties, good ion-exchange capacity, higher chemical, thermal stabilities, reproducibility and possessing good selectivity for heavy metals indicating its useful environmental applications. Few such excellent ion-exchange materials have been developed in our laboratory and successfully being used in environmental analysis [24-37]. In this chapter, the studies of ion-exchange properties on poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchange materials are described.

3.2 Experimental

3.2.1 Reagents and chemicals

Hydrochloric acid (HCl, 35%) and nitric acid (HNO_3, 35%) are obtained from E-Merck India Ltd. All other reagents and chemicals were of analytical reagent grade.

3.2.2 Instrumentation

- A water bath incubator shaker having a temperature variation of ± 0.5 °C was used for all equilibrium studies.
- An electronic balance (digital) - Sartorius (Japan), model 21 OS was used for weighing purpose.

3.2.3 Preparation of poly-o-toluidine Zr(IV) phosphate (POTZr(IV)P), poly-o-toluidine Ce(IV) phosphate (POTCe(IV)P) and Nylon-6,6 Sn(IV) phosphate (NySn(IV)P)

Various samples of POTZr(IV)P, POTCe(IV)P and NySn(IV)P were prepared following the method as given in Chapter–2 (section- 2.2.3). On the basis of Na^+ ion-exchange capacity and reproducibility, the samples S-5, T-4 and P-4 (Table 2.1, Table 2.2 and Table 2.3) were selected for the detail studies of their ion-exchange behavior.

3.3 Ion-exchange properties of POTZr(IV)P, POTCe(IV)P and NySn(IV)P composites

3.3.1 Ion-exchange capacity (IEC)

The ion-exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation-exchanger was determined by standard column process. One gram of the dry cation-exchangers (POTZr(IV)P, POTCe(IV)P) and NySn(IV)P sample S-5, T-4 and P-4 in the H^+-form were taken into a glass column having an internal diameter (i.d.) ~1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1M alkali and alkaline earth metal nitrates as eluants were used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~ 0.5 ml min^{-1}). The effluent was titrated against a standard (0.1M) NaOH solution for the total ions liberated in the solution using phenolphthalein indicator and the ion-exchange capacities (IEC) in meq g^{-1} are given in Table 3.1.

Table 3.1 Ion-exchange capacity of various exchanging ions on poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchangers

Exchanging ions	pH of the metal solutions	Ionic radii	Hydrated ionic radii	Ion-exchange capacity (meq g^{-1})		
				poly-o-toluidine Zr(IV) phosphate	poly-o-toluidine Ce(IV) phosphate	Nylon-6,6 Sn(IV) phosphate
Na^+	4.99	0.97	2.76	1.71	1.04	2.10
K^+	6.50	1.33	2.32	2.07	1.07	1.17
Li^+	3.30	0.68	3.40	0.95	0.75	0.95
Mg^{2+}	4.87	0.78	7.00	1.08	0.80	1.98
Ca^{2+}	6.20	1.06	6.30	1.64	0.64	1.70
Sr^{2+}	6.02	1.27	-	2.18	1.48	1.50
Ba^{2+}	6.50	1.43	5.90	1.36	1.16	1.36

3.3.2 Effect of eluant concentration

To find out the optimum concentration of the eluant for complete elution of H^+ ions, a fixed volume (250 ml) of sodium nitrate ($NaNO_3$) solution of varying concentrations were passed through a column containing 1g each of POTZr(IV)P, POTCe(IV)P and NySn(IV)P exchanger in the H^+-form with a flow rate of ~ 0.5 ml min^{-1}, in each case. The effluents were titrated against a standard alkali solution of 0.1M NaOH for the H^+ ions eluted out. The results are given in Table 3.2.

Table 3.2 Effect of eluant concentration on ion-exchange capacity of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchangers

S. No.	Poly-o-toluidine Zr(IV) phosphate		Poly-o-toluidine Ce(IV) phosphate		Nylon-6,6 Sn(IV) phosphate	
	Molar concentration of $NaNO_3$	Na^+ ion exchange capacity (meq g^{-1})	Molar concentration of $NaNO_3$	Na^+ ion exchange capacity (meq g^{-1})	Molar concentration of $NaNO_3$	Na^+ ion exchange capacity (meq g^{-1})
1	0.2	0.38	0.2	0.35	0.2	0.76
2	0.4	0.59	0.4	0.55	0.4	0.82
3	0.6	0.7	0.6	0.68	0.6	1.2
4	0.8	0.78	0.8	0.77	0.8	1.65
5	1.0	0.84	1.0	0.82	1.0	1.86
6	1.2	1.3	1.2	1.0	1.2	2.1
7	1.4	1.71	1.4	1.0	1.4	2.1
8	1.6	1.71	1.6	1.04	1.6	2.1
9	1.8	1.71	1.8	1.04	-	-

3.3.3 Elution behavior

Optimum concentration for complete elution for POTZr(IV)P composite cation-exchanger observed to be 1.4M, it was 1.6M for POTCe(IV)P while it was 1.2M for NySn(IV)P evident from Table 3.2. Two different columns containing 1g of each of the cation-exchanger in H^+- form were eluted with $NaNO_3$ solution of this concentration in different 10 ml fractions with minimum flow rate as described above and each fractions of 10 ml effluent were titrated against a standard alkali solution for the H^+ ions eluted out.

3.3.4 pH-titration

pH titration studies of poly-o-toluidine Zr(IV) phosphate (S-5), poly-o-toluidine Ce(IV) phosphate (T-4) nano-composites and fibrous Nylon-6,6 Sn(IV) phosphate cation-exchanger (P-4) were performed by the method of *Topp and Pepper* [38]. A total of 500 mg portions of the cation-exchanger in the H^+-form were placed in each of the several 250 ml conical flasks, followed by the addition of equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratio, the final volume is being 50 ml to maintain the ionic strength constant. The pH of the solution was recorded every 24

hours until equilibrium was attained which needed 5 days and pH at equilibrium was plotted against the milliequivalents of OH^- ions added.

3.3.5 Thermal effect on ion-exchange capacity (IEC)

To study the effect of temperature on the IEC, 1g samples of the composite cation-exchange materials (S-5, T-4 and P-4) in the H^+-form were heated at various temperatures in a muffle furnace for 1 hour and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature. The results are given in Table 3.3.

Table 3.3 Effect of temperature on ion-exchange capacity of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchanger on heating for 1 hour

S. No.	Heating temperature (°C)	Poly-o-toluidine Zr(IV) phosphate (S-5)		Poly-o-toluidine Ce(IV) phosphate (T-4)		Nylon-6,6 Sn(IV) phosphate (P-4)	
		Na^+ ion-exchange capacity (meq g^{-1})	% Retention of IEC	Na^+ ion-exchange capacity (meq g^{-1})	% Retention of IEC	Na^+ ion-exchange capacity (meq g^{-1})	% Retention of IEC
1	50	1.71	100	1.04	100	2.10	100
2	100	1.71	100	1.04	100	2.10	100
3	150	1.71	100	0.95	91.35	1.70	80.95
4	200	0.86	50.53	0.84	80.77	1.46	69.52
5	300	0.83	48.77	0.80	76.92	1.23	58.57
6	400	0.76	44.56	0.72	69.23	0.95	45.24
7	450	0.86	50.53	0.86	82.69	-	-
8	500	0.89	51.75	0.65	62.50	-	-
9	600	0.37	21.75	0.42	40.38	-	-
10	650	0.35	20.94	0.348	33.46	-	-
11	700	0.32	18.54	-	-	-	-

3.3.6 Selectivity (sorption) studies

The distribution coefficient (K_d values) of various metal ions on POTZr(IV)P, POTCe(IV)P and NySn(IV)P composite cation-exchangers were determined by batch method in various solvents systems. Various 200 mg portion's of the composite cation-exchanger beads (S-5, T-4 and P-4) in the H^+-form were taken in *Erlenmeyer* flasks with 20 ml of different metal nitrate solution in the required medium and kept for 24 hours

with continuous shaking for 6 hours in a temperature controlled incubator shaker at 25 ± 2°C to attain equilibrium. The initial metal ion concentration was so adjusted that it did not exceed 3% of its total ion-exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005 M solution of EDTA [39]. The alkali and alkaline earth metal ions [K^+, Na^+, Ca^{2+}] were determined by flame photometry and some heavy metal ions such as [Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}] were determined by atomic absorption spectrophotometry (AAS). The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase. In other word, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion-exchange material and hence mathematically can be calculated using the formula given as:

$$K_a = \frac{\text{m moles of metal ions / gm of ion - exchanger}}{\text{m moles of metal ions / ml of solution}} \ (\text{ml g}^{-1}) \qquad \text{.....3.1}$$

$$i.e. \quad K_d = (I-F)/F \times V/M \ (ml\,g^{-1}) \qquad \text{.....3.2}$$

where I is the initial amount of metal ion in the aqueous phase, F is the final amount of metal ion in the aqueous phase, V is the volume of the solution (ml) and M is the amount of cation-exchanger (g).

3.3.7 Separation factor

For the preferential uptake of metal ion, in the separation of a mixture of two metal ions, separation factor is determined. It can be defined and calculated as:

$$Separation\ factor\ (\alpha_B^A) = \frac{K_d(A)}{K_d(B)} \qquad \text{.....3.3}$$

Where K_d (A) and K_d (B) are the distribution coefficient for the two competing species A and B in the ion-exchange system. The separation factor is the preference of the ion-exchangers for one of the two counter ion species.

3.4 Ion-Exchange Kinetics

The kinetic behavior of cation-exchange material for the exchange of various metal ions was studied on the composite cation exchanger samples (S-5, T-4 and P-4) in the H^+ form.

3.4.1 Determination of infinite time of exchange

The infinite time of exchange is the time necessary to obtain equilibrium in an ion-

exchange process. The ion-exchange rate becomes independent of time after this time interval as evident from Figure 3.1, Figure 3.2 and Figure 3.3. About 35 minutes for sample S-5, 35 minute for sample T-4 and 40 minute for sample P-4 were required for the establishment of equilibrium at 30 °C, 35 °C and 30 °C for Mg^{2+} -H^{+} exchange. Similar behaviors were observed for Ca^{2+} -H^{+}, Sr^{2+} -H^{+}, Ba^{2+} -H^{+}, Ni^{2+} -H^{+}, Cu^{2+} -H^{+}, Mn^{2+} -H^{+}, and Zn^{2+} -H^{+} exchanges. Therefore 35, 35 and 40 minutes were assumed to be the infinite time of exchange for these studies.

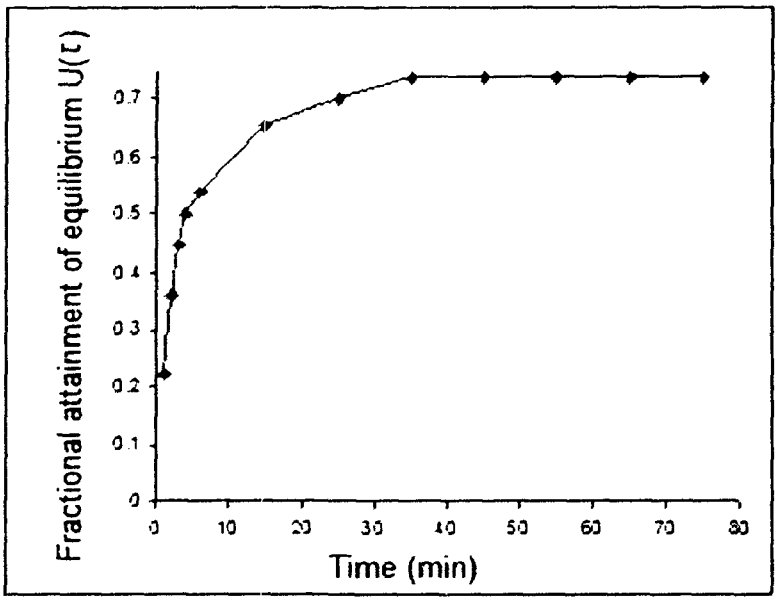


Figure 3.1 A plot of U(τ) vs time for M(II)- H(I) exchanges at 30 °C on poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger for the determination of infinite time

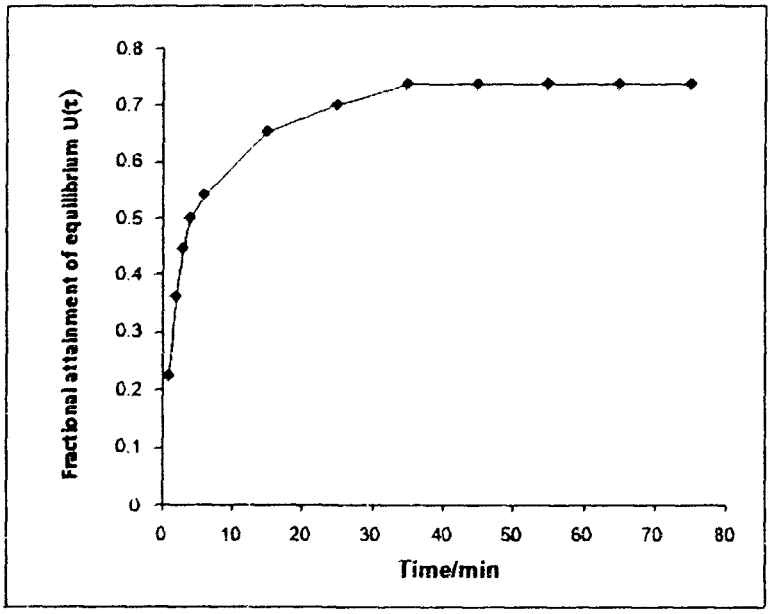


Figure 3.2 A plot of U(τ) vs time for M(II)- H(I) exchanges at 35 °C on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger for the determination of infinite time

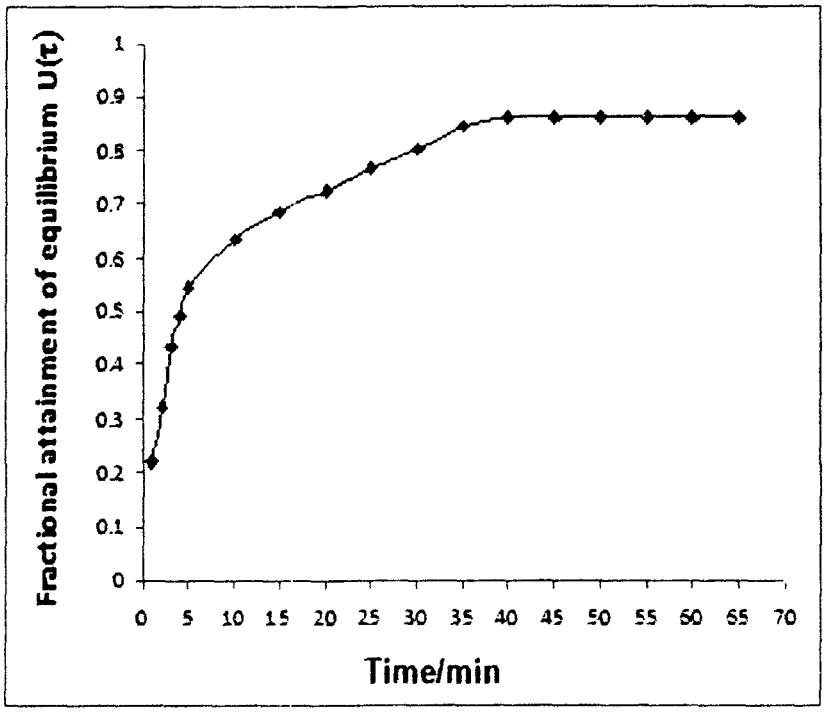


Figure 3.3 A plot of U(τ) vs time for M(II)- H(I) exchanges at 30 °C on Nylon-6,6 Sn(IV) phosphate composite cation-exchanger for the determination of infinite time

3.4.2 Kinetic measurements

The composite cation-exchange material samples (S-5, T-4 and P-4) were grounded and then sieved to obtain particles of definite mesh size (25-50, 50-70, 70-100 and100-125). Out of them the particles of mean radii ~125 μm (50-70 mesh) were selected to evaluate various kinetic parameters. The rate of exchange was determined by limited bath technique as follows:

Twenty milliliter fractions of the metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn and Zn) were shaken with 200 mg of the cation-exchangers in H^+-form in several Stoppard conical flasks at the desired temperatures for different time intervals (1.0, 2.0, 3.0 4.0 and 5.0 min). The supernatant liquid was removed immediately and determinations were made, usually by EDTA titration [40]. Each set was repeated four times and the mean value was taken for calculations.

3.4.3 Analytical procedures

The results are expressed in terms of the fractional attainment of equilibrium, $U(\tau)$ with time according to the equation

$$U(\tau) = \frac{\textit{the amount of exchange at time 't'}}{\textit{the amount of exchange at } \inf \textit{inite time}}. \qquad \text{.....3.4}$$

and the corresponding τ values were calculated by solving the Nernst-Plank equation [41,42].

3.5 Results and Discussion

Due to the high percentage of yield, better ion-exchange capacity, reproducible behavior, chemical and thermal stabilities, poly-o-toluidine Zr(IV) phosphate (S-5, Table 2.1), poly-o-toluidine Ce(IV) phosphate (T-4, Table 2.2) and Nylon-6,6 Sn(IV) phosphate (P-4, Table 2.3) were chosen for detail ion-exchange studies.

The effect of the size and charge of the exchanging ions on the ion-exchange capacity were also observed for these materials. The ion-exchange capacity of the composite cation-exchangers for alkali metal ions and alkaline earth metal ions increased according to the decrease in their hydrated ionic radii Table 3.1.

The column elution experiments indicated the dependence of the concentration of the eluant on the rate of elution which is a usual behavior for such materials. The minimum molar concentration of $NaNO_3$ as eluent for S-5 was found 1.4 M, 1.6 M for T-4 while 1.2 M for P-4 for maximum release of H^+ ions from 1 g of the cation exchanger as evident from the Figure 3.4a, Figure 3.4b and Figure 3.4c.

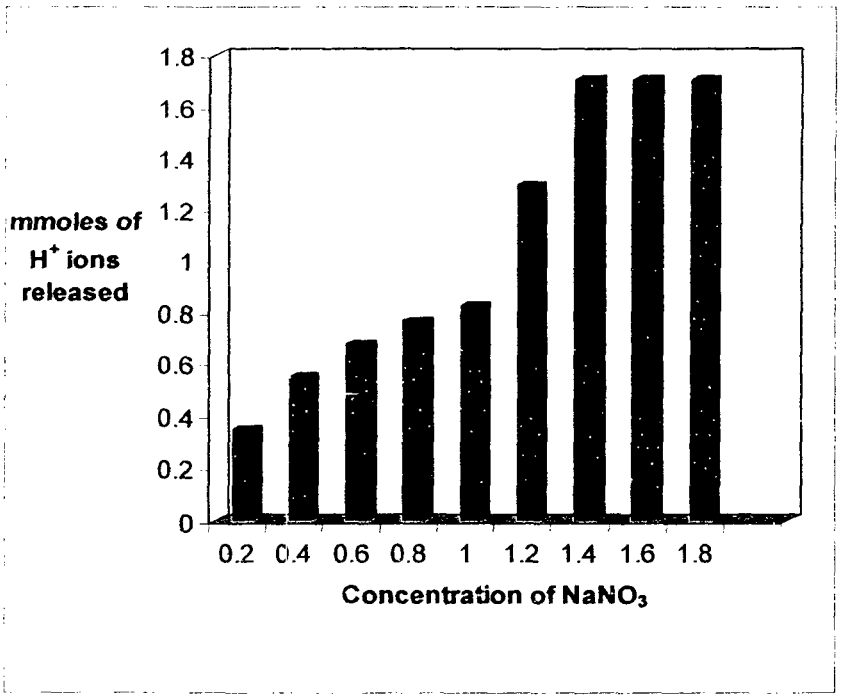


Figure 3.4a Concentration plot of poly-o-toluidine Zr(IV) phosphate

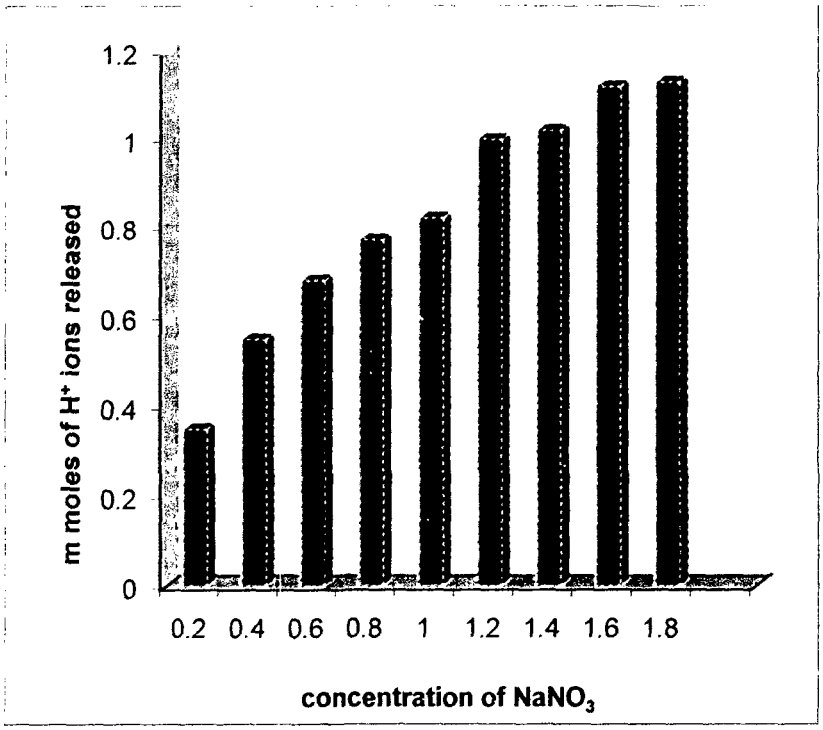


Figure 3.4b Concentration plot of poly-o-toluidine Ce(IV) phosphate

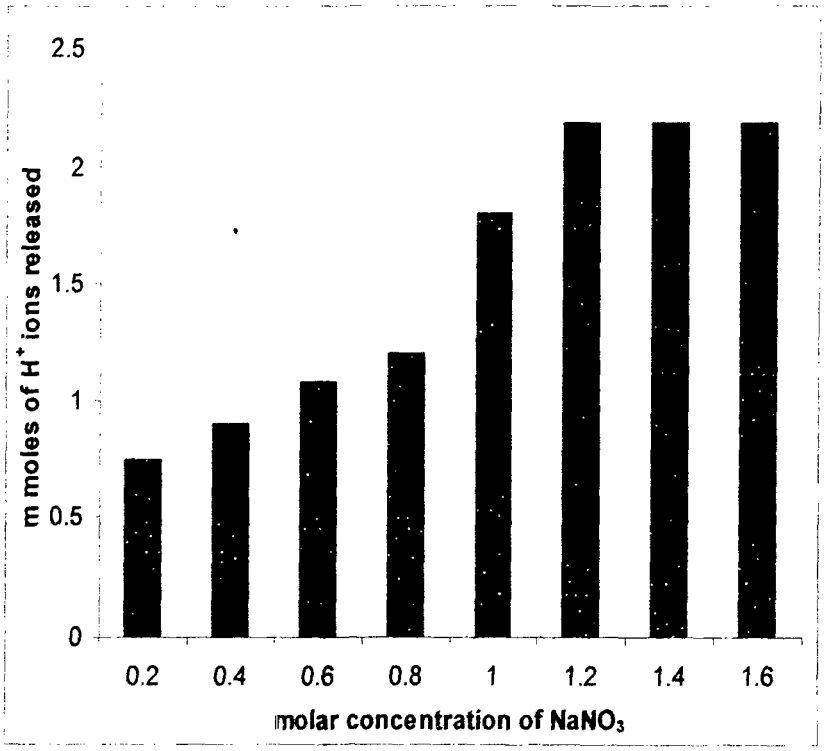


Figure 3.4c Concentration plot of Nylon-6,6 Sn(IV) phosphate

The elution behavior indicates that the exchange is quite fast because upto 250 ml of sodium nitrate solution is enough to release the total H^+ from 1g sample of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate cation-exchange materials (Figure 3.5a, Figure 3.5b and Figure 3.5c)

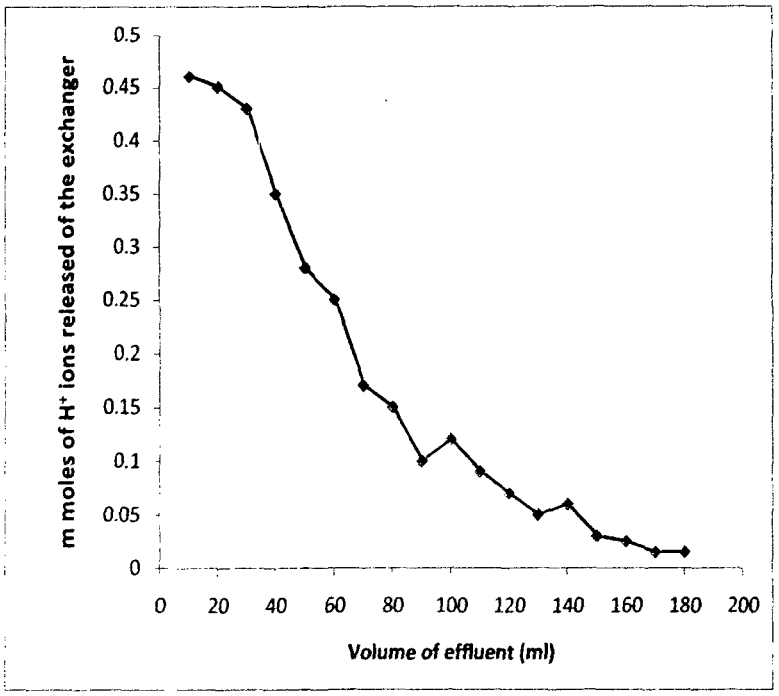


Figure 3.5a The elution behavior of poly-o-toluidine Zr (IV) phosphate cation-exchange material

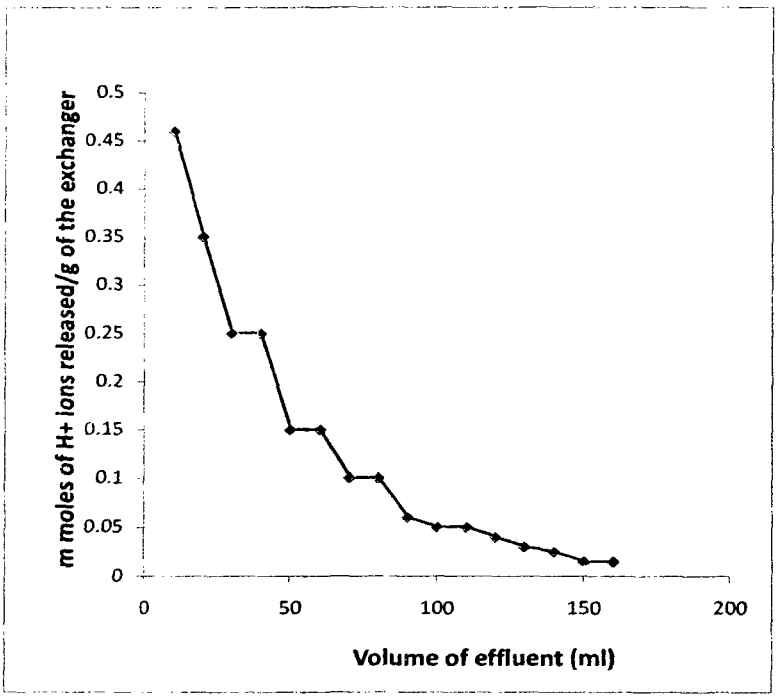


Figure 3.5b The ellution behavior of poly-o-toluidine Ce(IV) phosphate cation-exchange material

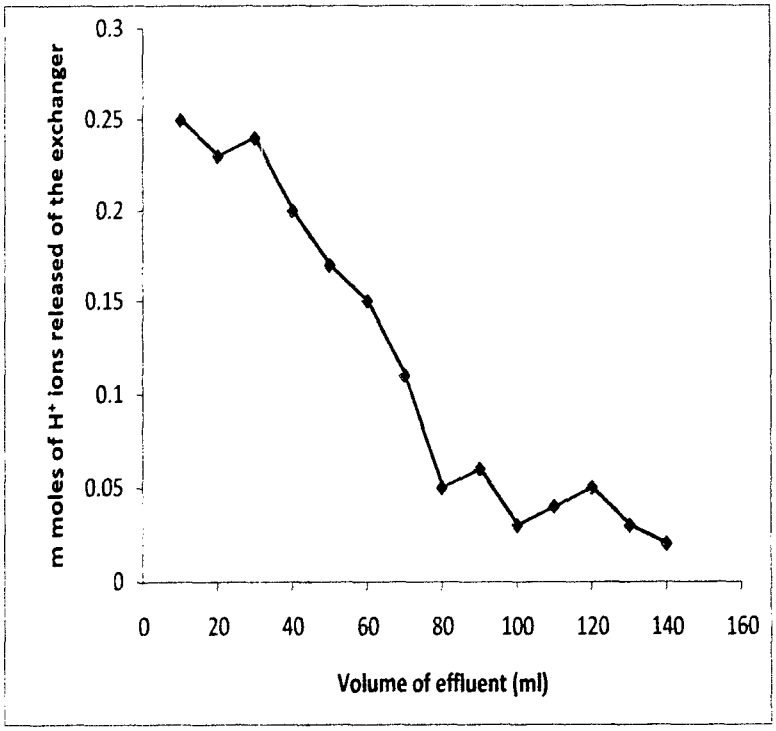


Figure 3.5c The ellution behavior of Nylon-6,6 Sn(IV) phosphate cation-exchange material

3.5.1 pH titration

The pH titration curves for poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate were obtained under equilibrium conditions with NaOH/NaCl, KOH/KCl and LiOH/LiCl. The systems indicated bifunctional behavior of the materials as shown in Figure 3.6a, Figure 3.6b and Figure 3.6c. The composite materials poly-o-toluidine Zr(IV) phosphate (S-5), poly-o-toluidine Ce(IV) phosphate (T-4) and Nylon-6,6 Sn(IV) phosphate (P-4) appear to be strong cation exchangers as indicated by low pH (~2.2), (~2.0) and (~3.6) of the solutions respectively, when no OH^- added to the system. For the samples (S-5, T-4 and P-4), the rate of H^+-K^+ exchange was faster than those of H^+-Na^+ and H+-Li+ exchanges. The adsorption behavior of alkali metals on the materials, for poly-o-toluidine Zr(IV) phosphate (S-5) was observed to be in the order of Na(I) >Li(I) >K(I) while poly-o-toluidine Ce(IV) phosphate (T-4) and Nylon-6,6 Sn(IV) phosphate (P-4) were observed to be in the order of K(I) > Na(I) >Li(I).

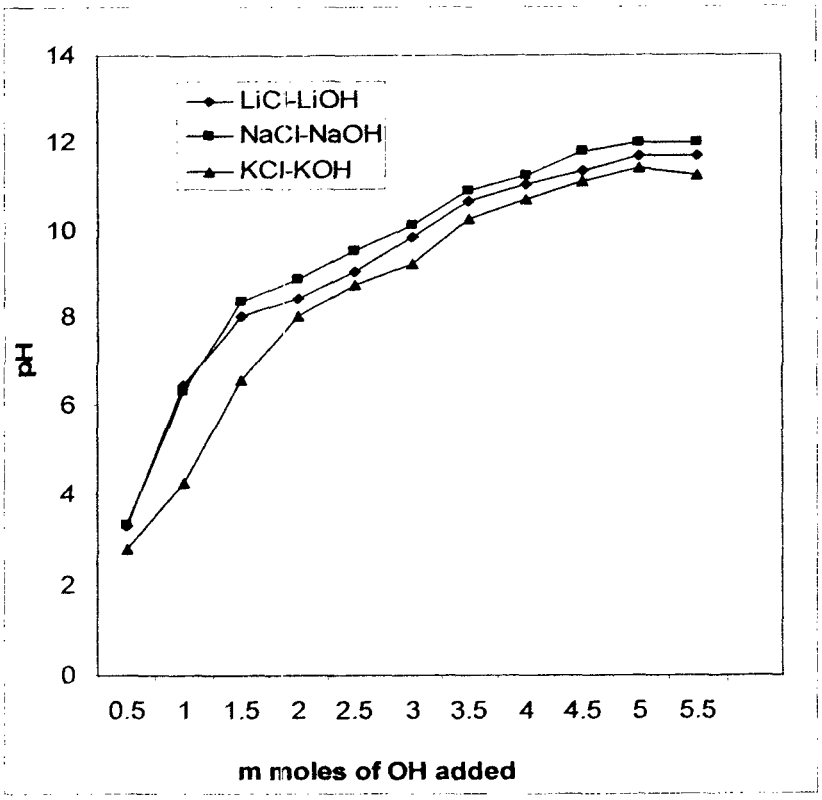


Figure 3.6a pH-titration curves for poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger

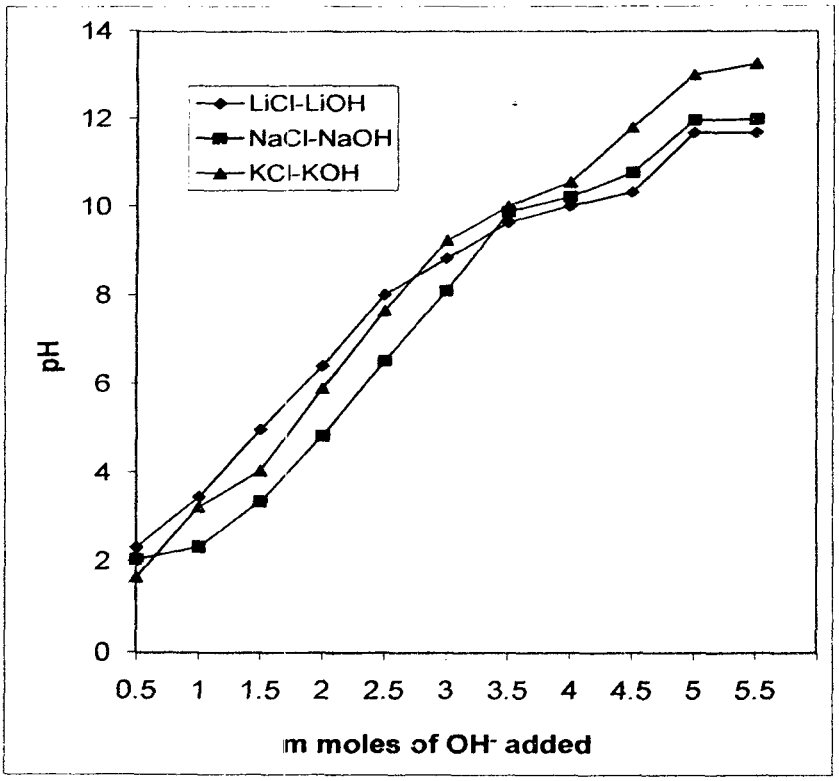


Figure 3.6b pH-titration curves for poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger

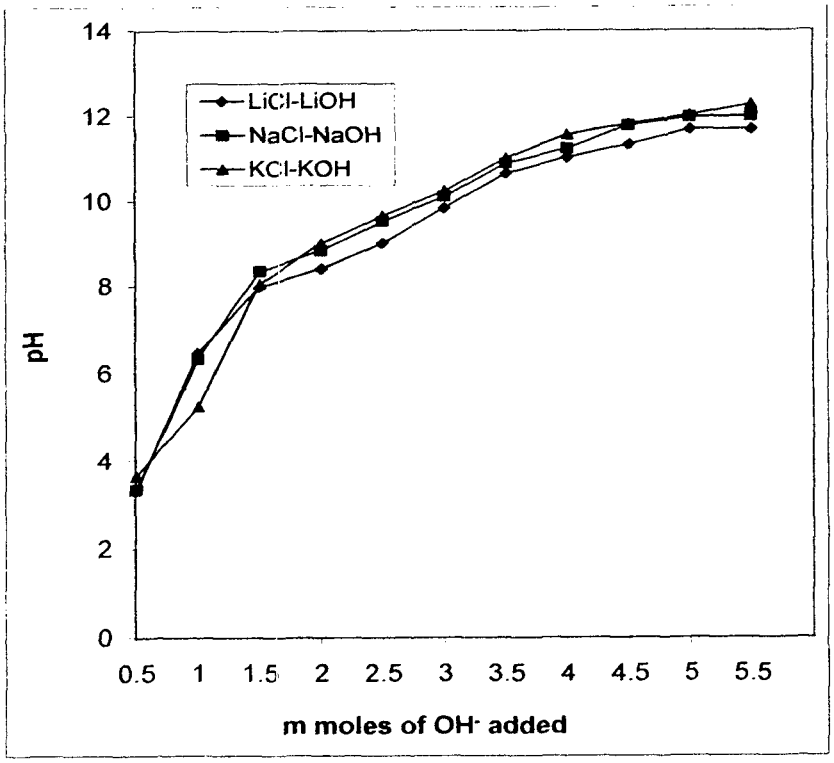


Figure 3.6c pH-titration curves for Nylon-6,6 Sn(IV) phosphate fibrous composite cation-exchanger

3.5.2 Thermal effect on ion-exchange capacity

On heating at different temperatures for one hour, the ion-exchange capacity of the dried composite cation-exchanger samples (S-5, T-4 and P-4) decreased as the temperature increased (Table 3.3). The ion-exchange capacity of the poly-o-toluidine Zr(IV) phosphate material was found to be stable upto 200 °C and it retained about 50.53% of the initial ion-exchange capacity by heating upto 300 °C, in case of ion-exchange capacity of the material of poly-o-toluidine Ce(IV) phosphate, it was found to be nearly stable upto 150 °C and it retained about 80.77% of the initial ion-exchange capacity by heating upto 300 °C while in case of ion-exchange capacity of Nylon-6,6 Sn(IV) phosphate, it was found to be nearly stable upto 150 °C and it retained about 69.52% of the initial ion-exchange capacity by heating upto 200 °C.

3.5.3 Selectivity studies

In order to find out the potentiality of these composite cation-exchange material samples S-5, T-4 and P-4, in the separation of metal ions, distribution studies for several metal ions were performed in different solvent systems. It is apparent from the data given in Table 3.4, Table 3.5 and Table 3.6 that the K_d-values can vary with the composition and

nature of the contacting solvents. It was observed from the K_d-values of poly-o-toluidine Zr(IV) phosphate (S-5, Table 3.4) in pH 5.75, 10% Acetone and 1×10^{-1} M H_2SO_4 solvent systems; Hg^{2+} was strongly adsorbed on the surface of ion-exchange material while Zn^{2+}, Ba^{2+}, Sr^{2+} and Fe^{3+} are significantly adsorbed and the remaining are partially adsorbed. It was also observed from the distribution studies (K_d-values) of poly-o-toluidine Ce(IV) phosphate (T-4, Table 3.5) that Cd^{2+} was highly adsorbed while Hg^{2+}, Ca^{2+} and Ba^{2+} are significantly adsorbed and the remaining are partially adsorbed. It was observed from the distribution studies (K_d-values) of Nylon-6,6 Sn(IV) phosphate (P-4, Table 3.6) that Hg^{2+} was highly adsorbed while Pb^{2+}, Fe^{3+} , $Mg^{2+}$and Sr^{2+} are significantly adsorbed and the remaining are partially adsorbed. Thus, we can say that the composite cation-exchangers sample S-5, T-4 and P-4 are highly selective for Hg^{2+} and Cd^{2+} ions and can be very well utilized for the determination and separation of mercury and cadmium from waste effluents.

Table 3.4 K_d-values of some metal ions on poly-o-toluidine Zr(IV) phosphate nano-composite cation exchanger column in different solvent systems

Metal ions	Pb^{2+}	Hg^{2+}	Cu^{2+}	Co^{2+}	Cd^{2+}	Zn^{2+}	Ni^{2+}	Mn^{2+}	Fe^{3+}	Al^{3+}	Ba^{2+}	Zr^{4+}	Th^{2+}	Sr^{2+}
DMW	116	**476**	200	67	157	1900	60	150	233	44	150	125	150	83
0.1 M HCl	40	-	11	5	54	23	25	-	275	200	37	100	33	20
0.01 M HCl	55	-	16	25	60	45	77	100	66	60	50	100	750	46
0.1M HNO_3	40	**715**	12	16	30	31	133	100	300	400	40	600	166	6
0.01M HNO_3	50	**433**	75	66	60	23	175	350	42	45	380	100	233	30
10% Formic acid	38	-	13	24	-	-	60	-	150	66	-	75	-	-
20% Formicacid	81	**130**	-	59	-	-	30	-	166	233	-	66	-	-
30% Formicacid	114	-	6	59	-	-	55	-	200	133	-	33	-	-
10% Ethanol	114	**585**	233	100	200	100	200	200	225	23	550	100	100	54
20% Ethanol	54	**520**	166	66	172	114	60	200	66	60	175	66	150	100
10% Acetone	116	**1560**	233	47	133	100	50	22	125	114	333	80	300	100
pH3.75	200	**357**	233	66	325	172	150	-	100	40	366	40	50	157
pH5.75	16	**1820**	45	63	233	100	60	150	400	150	242	100	75	171
0.1 M H_2SO_4	40	**1083**	17	108	23	7	66	-	250	-	220	100	150	220
0.01M H_2SO_4	133	**520**	37	81	36	23	55	44	100	66	100	75	-	100

Table 3.5 K_d-values of some metal ions on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger column in different solvent systems

Metal ion / Solvents	Fe^{2+}	Ba^{2+}	Pb^{2+}	Ni^{2+}	Hg^{2+}	Ca^{21+}	Sr^{2+}	Cr^{2+}	Cu^{2+}	Cd^{2+}	Zn^{2+}
DMW	100	50	33	25	33	120	18	16	100	**170**	25
0.1M HNO_3	50	13	42	67	221	70	47	88	212	**450**	35
0.01M HNO_3	120	55	112	45	65	55	65	33	230	**340**	270
0.001M HNO_3	105	69	65	200	45	420	55	58	14	**214**	120
0.1M HClO4	125	100	168	132	150	26	11	100	39	**320**	220
0.01M HClO4	30	120	100	98	-	49	143	58	79	**350**	150
0.001M HClO4	58	43	37	200	19	60	45	85	12	**500**	210
0.1M HCl	269	90	15	66	63	42	70	32	-	**50**	90
0.01M HCl	90	120	33	08	50	80	45	50	350	**970**	120
0.001M HCl	23	40	42	96	27	45	61	87	99	**875**	133
10% DMSO	13	124	18	20	301	100	90	65	170	**458**	90
10% Formic acid	205	20	-	15	70	125	170	125	90	**180**	-
Buffer 10	122	200	150	66	240	100	18	35	240	**550**	200
0.1M H_2SO_4	40	133	66	7	59	10	67	43	150	**120**	-

Table 3.6 K_d -values of some metal ions on Nylon-6,6 Sn(IV) phosphate cation-exchanger column in different solvent systems

Metal ions	Pb^{2+}	Hg^{2+}	Cu^{2+}	Co^{2+}	Cd^{2+}	Zn^{2+}	Ni^{2+}	Mg^{2+}	Fe^{3+}	Al^{3+}	Ba^{2+}	Sr^{2+}
DMW	62	**50**	25	67	43	41	60	150	60	25	33	83
10^{-1} mol dm^{-3} HNO_3	33	**270**	17	5	21	23	25	7	11	150	6	20
10^{-2} mol dm^{-3} HNO_3	20	**40**	15	25	7	45	7	-	14	20	-	46
10^{-3} mol dm^{-3} HNO_3	27	**170**	33	16	25	31	33	10	14	25	50	6
10^{-1} mol dm^{-3} HCl	114	**200**	8	66	29	23	75	6	10	200	9	30
10^{-2} mol dm^{-3} HCl	8	**75**	15	24	31	-	6	-	25	17	88	41
10^{-3} mol dm^{-3} HCl	33	**30**	25	59	50	33	30	-	100	11	233	25
10^{-1} mol dm^{-3} $HClO_4$	88	**25**	15	47	27	11	55	25	10	200	-	50
10^{-2} mol dm^{-3} $HClO_4$	22	**78**	33	15	36	21	20	6	11	30	41	24
10^{-3} mol dm^{-3} $HClO_4$	88	**50**	15	33	64	27	26	-	80	10	24	100
10^{-1} mol dm^{-3} H_2SO_4	100	**23**	27	25	15	10	50	22	-	50	100	17
10% Ethanol	50	**150**	31	9	50	14	15	14	200	200	67	14
10% Acetone	86	**180**	23	11	25	7	60	7	120	50	29	33

3.5.4 Separation factor

The separation factor is the proportion of the concentration ratios of the counter ions in the ion-exchanger and the solution. If the ion A is preferred, the factor (α_B^A) is larger then unity, and if B is preferred, the factor is smaller then unity. The numerical values of the separation factor (dimension less) are not affected by the choice of the concentration unit. Of course, the separation factor is usually not constant, but depends on the total concentration of the solution, the temperature and equivalent fraction. On the basis of K_d values separation factor for some metal ions are given in Table 3.7, Table 3.8 and Table 3.9. The values of separation factor clarify that the separation is feasible and can be achieved easily.

Table 3.7 Separation factor of different metal ions on poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchange material

Separation factor	DMW	1×10^{-2} M HCl	10% Acetone
α_{Pb}^{Hg}	4.10	17.88	13.448
α_{Cd}^{Hg}	3.03	23.83	11.729
α_{Co}^{Hg}	7.104	44.69	33.19
α_{Al}^{Hg}	3.17	7.15	70.91
α_{Mg}^{Hg}	10.82	1.79	13.68
α_{Fe}^{Hg}	2.04	2.38	12.48
α_{Cu}^{Hg}	2.38	59.58	6.695

Table 3.8 Separation factor of different metal ions on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchange material

Separation factor	DMW	1×10^{-3} $HClO_4$	1×10^{-3} M HCl
α_{Cu}^{Cd}	1.70	41.66	8.84
α_{Fe}^{Cd}	1.70	8.62	38.04
α_{Hg}^{Cd}	5.15	26.32	32.41
α_{Pb}^{Cd}	5.15	13.51	20.83
α_{Ni}^{Cd}	6.50	2.50	9.11
α_{Zn}^{Cd}	31.25	47.64	30.83
α_{Sr}^{Cd}	9.44	11.11	14.34
α_{Ba}^{Cd}	3.40	11.63	21.88

Table 3.9 Separation factor of different metal ions on Nylon-6,6 Sn(IV) phosphate composite cation-exchange material

Separation factor	1×10^{-1} M HNO_3	1×10^{-1} M HCl	1×10^{-2} M $HClO_4$
α_{Pb}^{Hg}	8.18	1.75	3.545
α_{Co}^{Hg}	54.0	3.03	5.20
α_{Ni}^{Hg}	10.8	2.667	3.90
α_{Mg}^{Hg}	38.57	33.33	13.0
α_{Cd}^{Hg}	12.857	6.897	2.167
α_{Fe}^{Hg}	24.545	20.0	7.09
α_{Al}^{Hg}	1.80	0	2.60
α_{Cu}^{Hg}	15.88	25.0	2.36

3.6 Ion-Exchange Kinetic Studies on Poly-o-toluidine Zr(IV) phosphate, Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate Composite Materials

Kinetic measurements were made under conditions favouring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Mg(II)–H(I), Ca(II)–H(I), Sr(II)–H(I), Ba(II)–H(I), Ni(II)–H(I), Cu(II)–H(I), Mn(II)–H(I) and Zn(II)–H(I). The particle diffusion controlled phenomenon is favoured by a high metal ion concentration, a relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture.

The infinite time of exchange is the time necessary to obtain equilibrium in an ion-exchange process. The ion-exchange rate becomes independent of time after this interval. Figure 3.1, Figure 3.2 and Figure 3.3 shows that 35, 35 and 40 min were required for the establishment of equilibrium at 30 °C, 35 °C and 30 °C for Mg^{2+}–H^+ exchange for poly-o-toluidine Zr(IV) phosphate (S-5), poly-o-toluidine Ce(IV) phosphate (T-4) and Nylon-6,6 Sn(IV) phosphate (P-4) respectively. Similar behavior was observed for Ca^{2+}–H^+, Sr^{2+}–H^+, Ba^{2+}–H^+, Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+ exchanges. Therefore, 35 min, 35 min and 40 min were assumed to be the infinite time of exchange for the systems.

A study of the concentration effect on the rate of exchange at 30 °C and 35 °C showed that the initial rate of exchange was proportional to the metal ion concentration at and above 0.03 M for poly-o-toluidine Zr(IV) phosphate, S-5 (Figure 3.7), 0.03 M for poly-o-toluidine Ce(IV) phosphate, T-4 (Figure 3.8) and 0.04 M for Nylon-6,6 Sn(IV)

phosphate, P-4 (Figure 3.9). Below the concentration of 0.02 M, film diffusion control was more prominent for the materials.

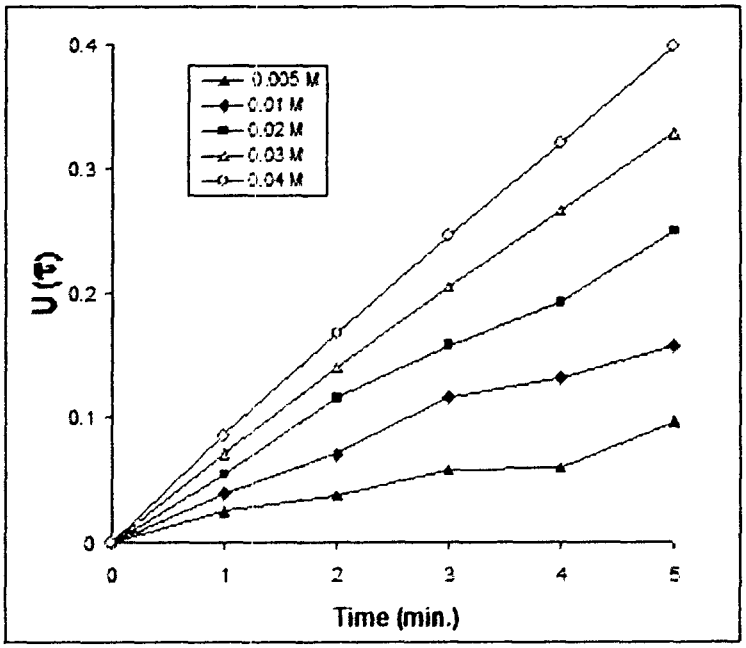


Figure 3.7 A plot of τ versus t (time) for M(II)- H(I) exchanges at 30 °C on a poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger using different metal solution concentration

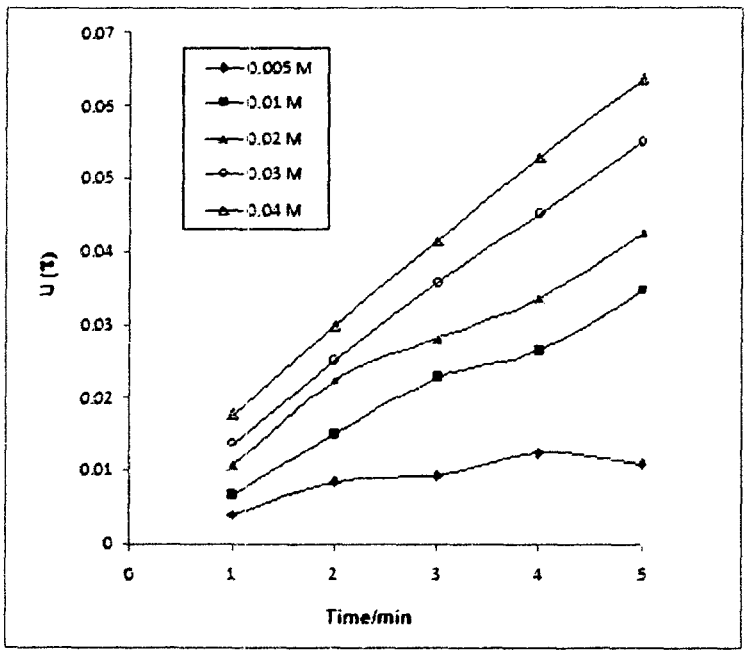


Figure 3.8 A plot of τ versus *t* (time) for M(II)–H(I) exchanges at 35 °C on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger using different metal solution concentration

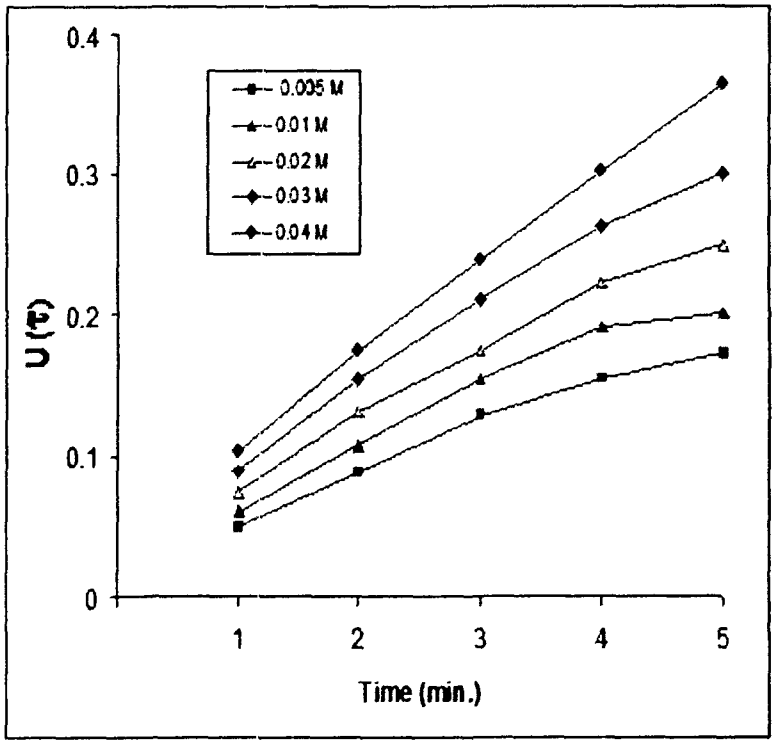


Figure 3.9 A plot of τ versus *t* (time) for M(II)–H(I) exchanges at 30 °C on Nylon-6,6 Sn(IV) phosphate composite cation-exchanger using different metal solution concentration

Plots of $U(\tau)$ versus t (min), for all metal ions (Figure 3.10, Figure 3.11 and Figure 3.12) indicated that the fractional attainment of equilibrium was faster at a higher temperature suggesting that the mobility of the ions increased with the increase in temperature and the uptake decreased with time. Each value of $U(\tau)$ will have a corresponding value of τ, a dimensionless time parameter.

On the basis of the Nernst–Planck equation, the numerical results can be expressed by explicit approximation [43-45].

$$U(\tau) = \left\{1 - \exp\left[\pi^2\left(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3\right)\right]\right\}^{1/2} \quad \text{.....3.5}$$

where τ is the half time of exchange= $\bar{D}_{H^+} t / r_o^2$, α is the mobility ratio = $\bar{D}_{H^+} / \bar{D}_{M^{2+}}$, r_0 is the particle radius, $\bar{D}_{H^+}$ and $\bar{D}_{M^{2+}}$ are the inter diffusion coefficients of counter ions

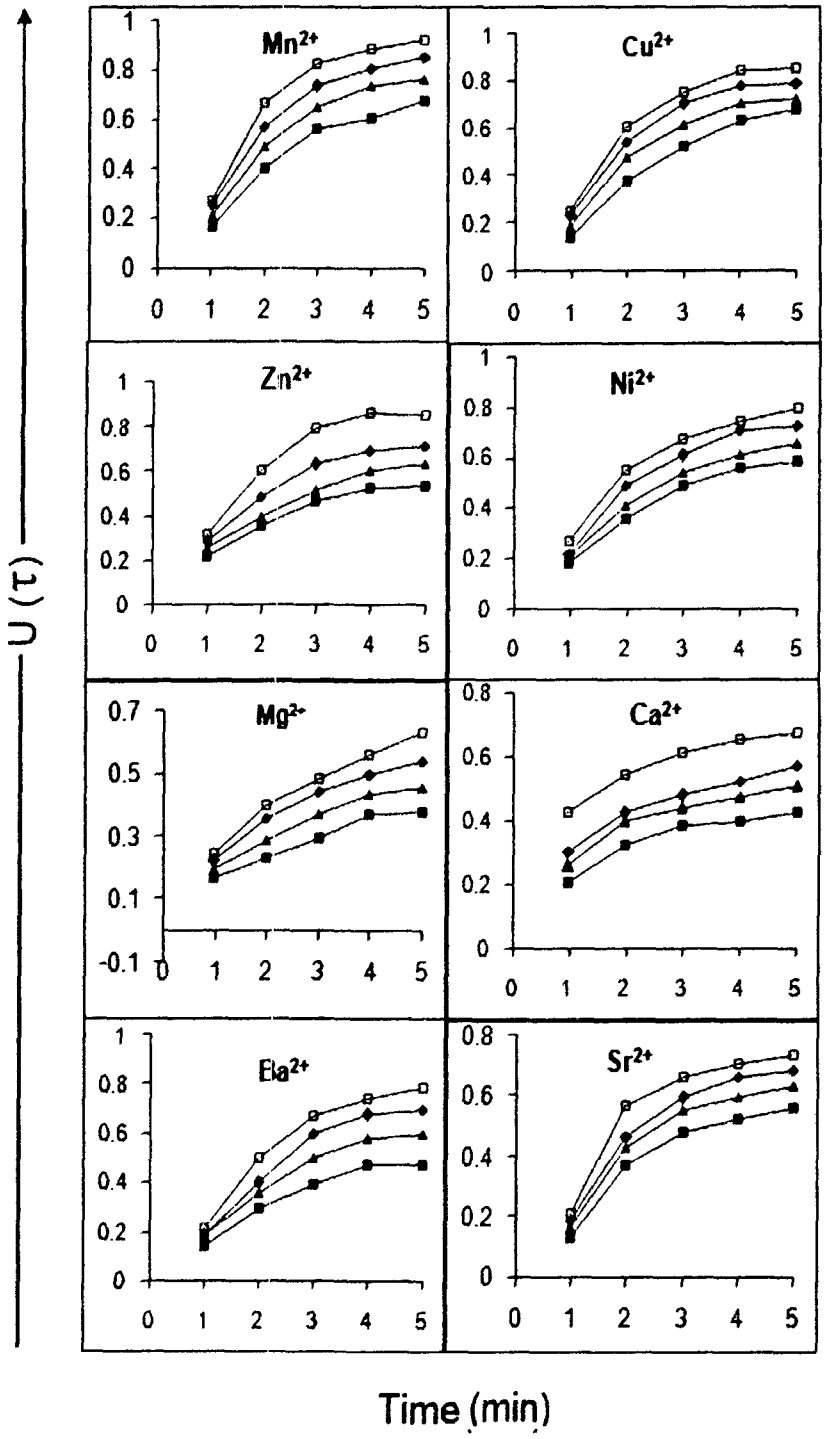


Figure 3.10 Plots of U(τ) versus t (time) for different M(II)- H(I) exchanges at different temperature: (■) 30 °C; (▲) 45 °C; (♦) 60 °C; (□) 75 °C on poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger

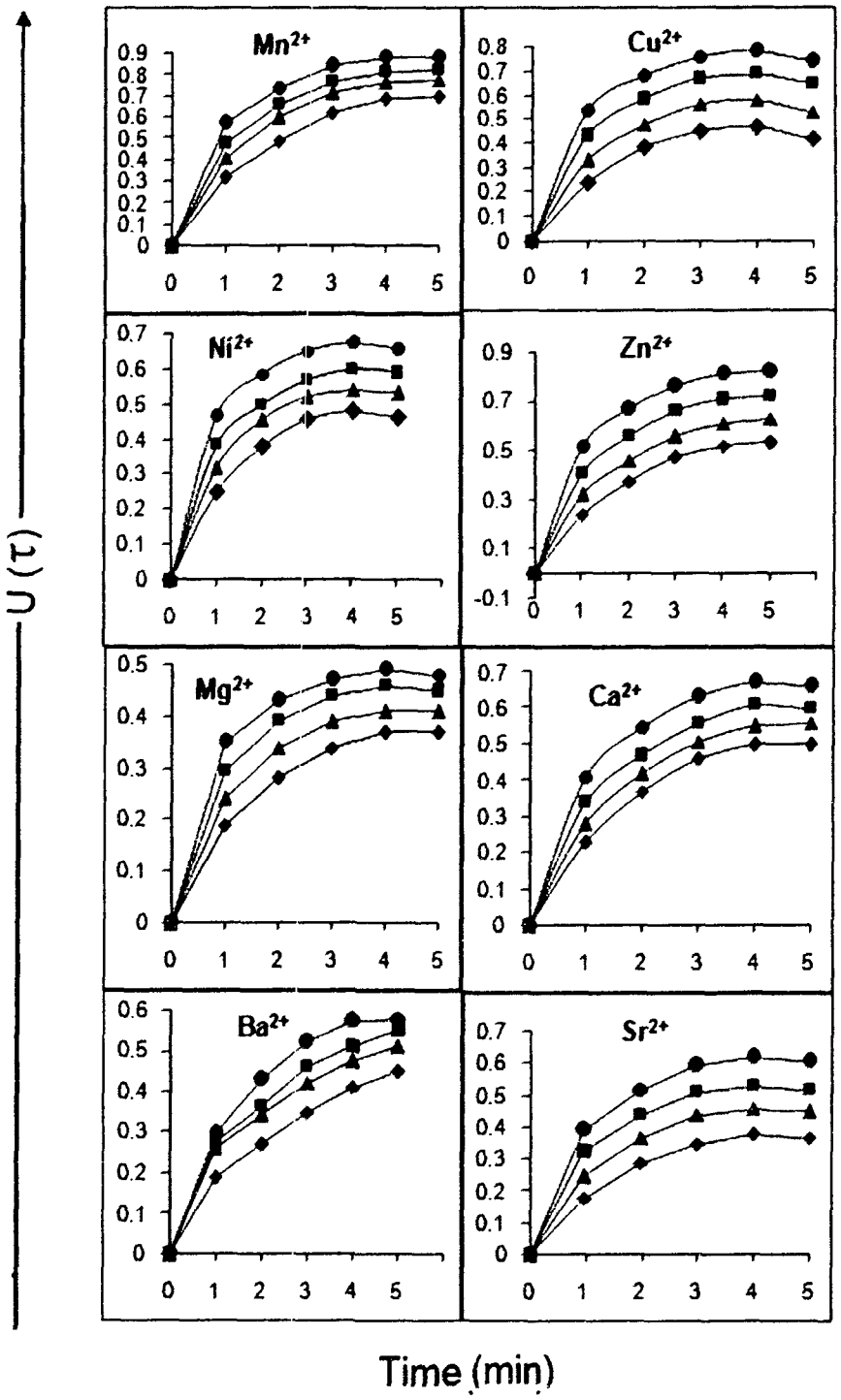


Figure 3.11 Plots of $U(\tau)$ vs. t (time) for different M(II)–H(I) exchanges at different temperature: (♦) 25 °C; (▲) 35 °C; (■) 50 °C; (●) 65 °C on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger

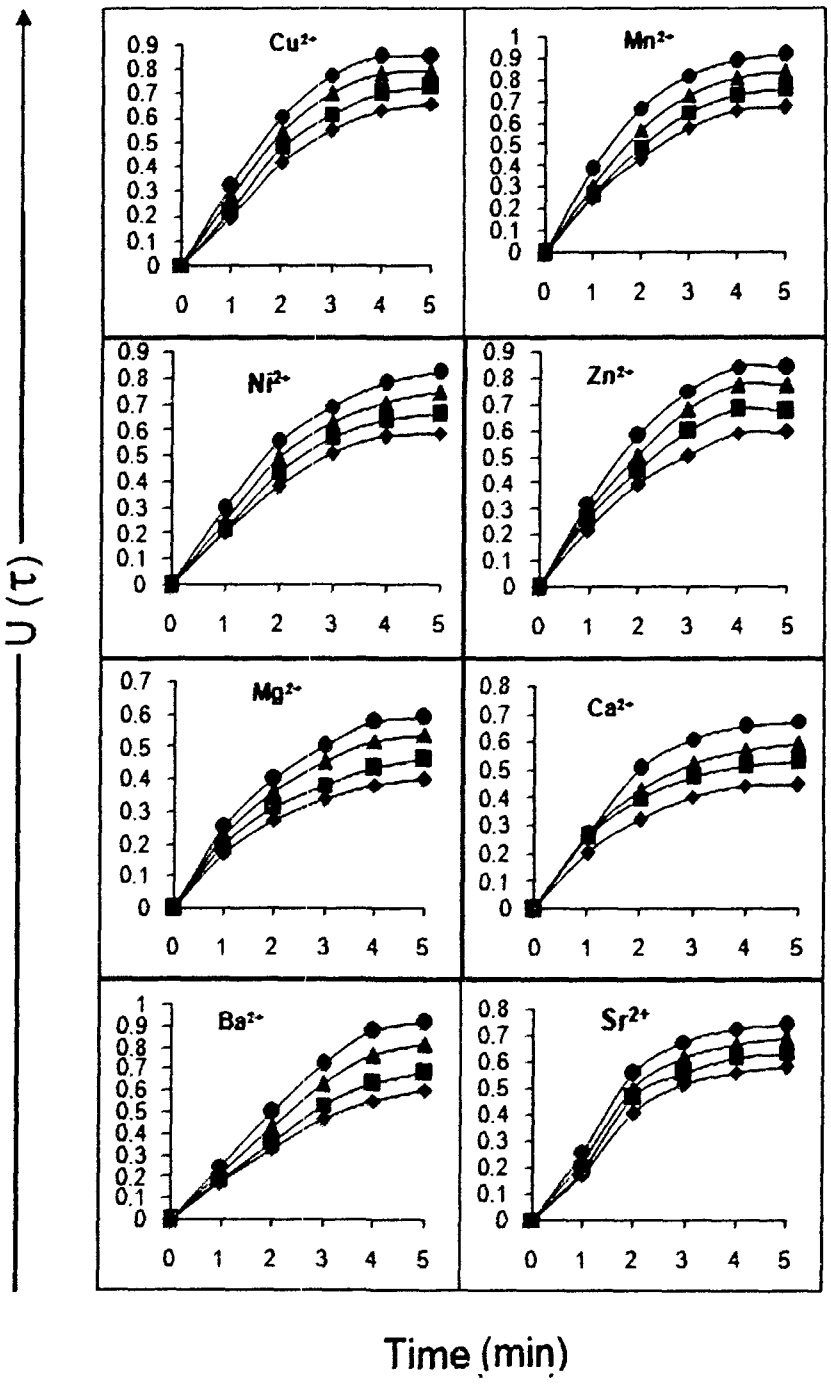


Figure 3.12 Plots of $U(\tau)$ vs. t (time) for different M(II)–H(I) exchanges at different temperature: (♦) 30 °C; (■) 45 °C; (▲) 60 °C; (●) 75 °C on Nylon-6,6 Sn(IV) phosphate composite cation-exchanger

H^+ and M^{2+} respectively in the exchanger phase. The three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ depend upon the mobility ratio (α) and the charge ratio ($Z_{H^+}/Z_{M^{2+}}$) of the exchanging ions. Thus they have different expressions as given below. When the exchanger is taken in the H^+ form and the exchanging ion is M^{2+}, for $1 \leq \alpha \leq 20$, as in the present case, the three functions have the values:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}}, \qquad \text{.....3.6}$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}}; \qquad \text{.....3.7}$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.140}} \qquad \text{.....3.8}$$

Each value of $U(\tau)$ will have a corresponding value of τ which is obtained on solving Eq. (3.5) using a computer. The plots of τ versus time (t) at the four temperatures, as shown in Figure 3.13, Figure 3.14 and Figure 3.15 are straight lines passing through the origin, confirming the particle diffusion control phenomenon for M(II)–H(I) exchanges at a metal ion concentration of 0.03 M for poly-o-toluidine Zr(IV) phosphate (S-5), concentration is 0.03 M for poly-o-toluidine Ce(IV) phosphate and 0.04 M for Nylon-6,6 Sn(IV) phosphate.

The slopes (S values) of various τ versus time (t) plots are given in Table 3.10, Table 3.11 and Table 3.12.

The S values are related to $\bar{D}_{H^+}$ as follows:

$$S = \bar{D}_{H^+}/r_0^2, \qquad \text{.....3.9}$$

The values of $-\log \bar{D}_{H^+}$ obtained by using Eq. (3.9) plotted against 1000/ T(K) are straight lines as shown in Figure 3.16, Figure 3.17 and Figure 3.18, thus verifying the validity of the Arrhenius relation;

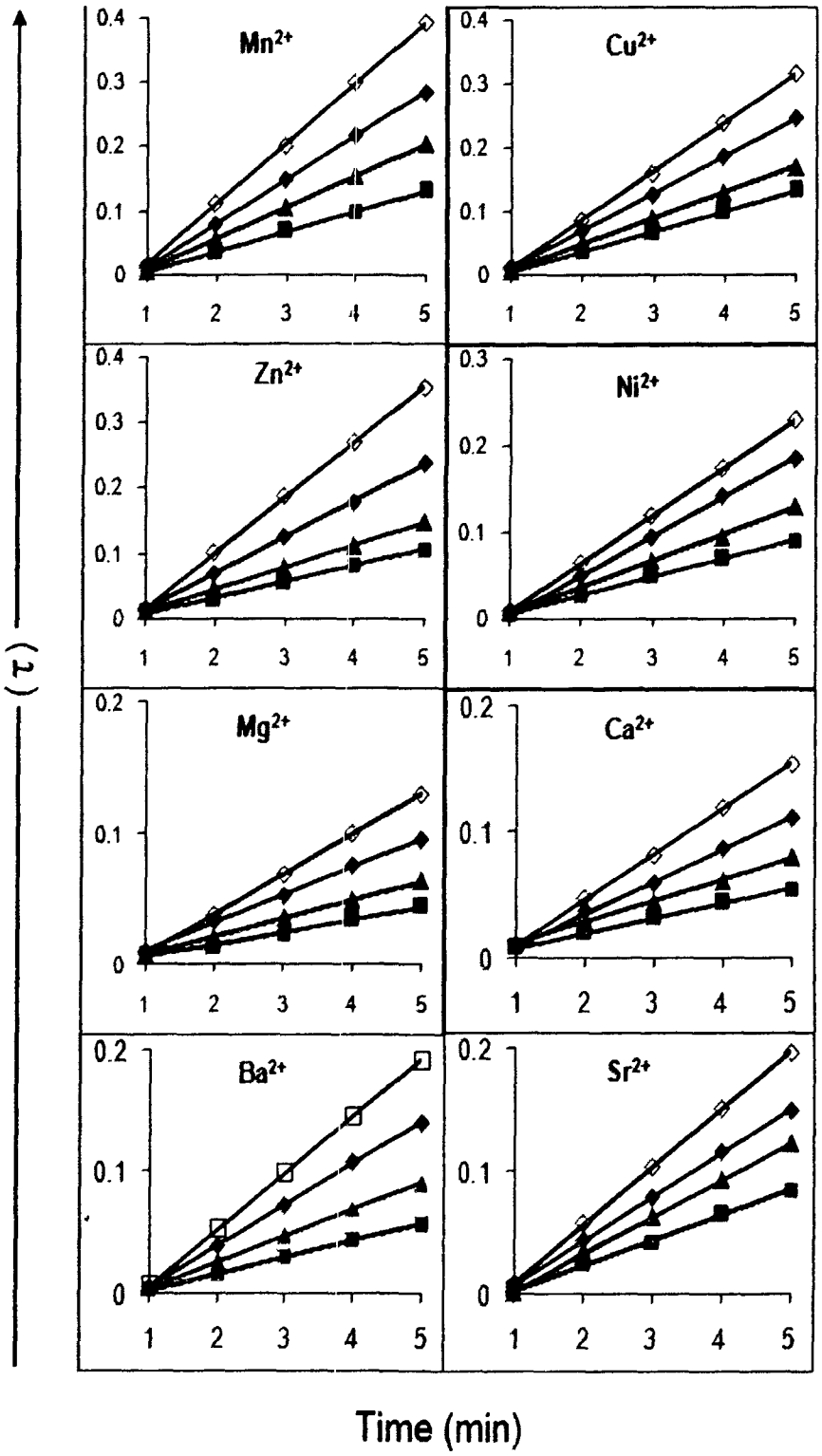


Figure 3.13 Plots of τ versus t (time) for different M(II)- H(I) exchanges at different temperature: (■) 30 °C; (▲) 45 °C; (♦) 60 °C; (□) 75 °C on poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger

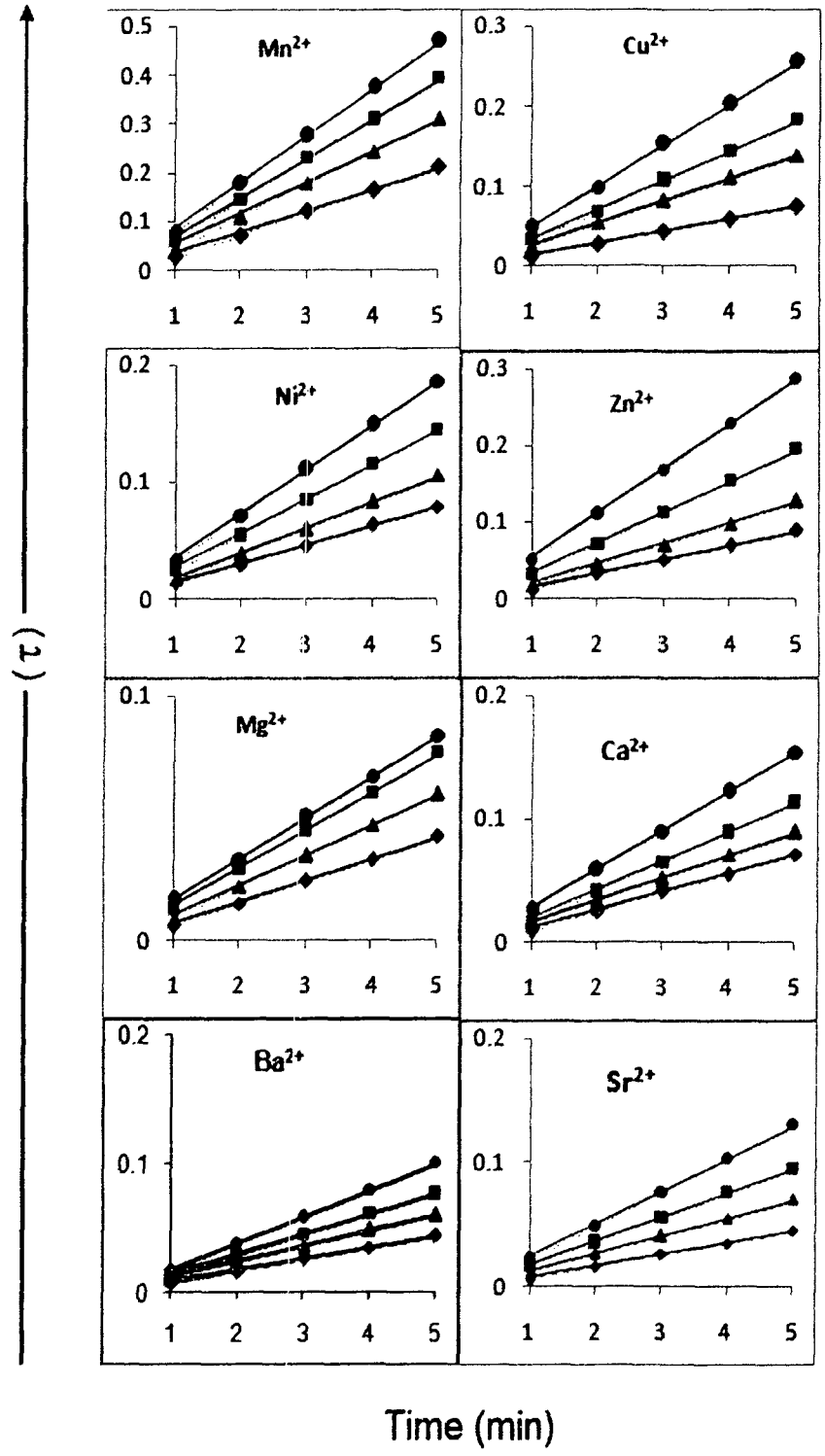


Figure 3.14 Plots of τvs. *t* (time) for different M(II)–H(I) exchanges at different temperature: (♦) 25 °C; (▲) 35 °C; (■) 50 °C; (●) 65 °C on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger

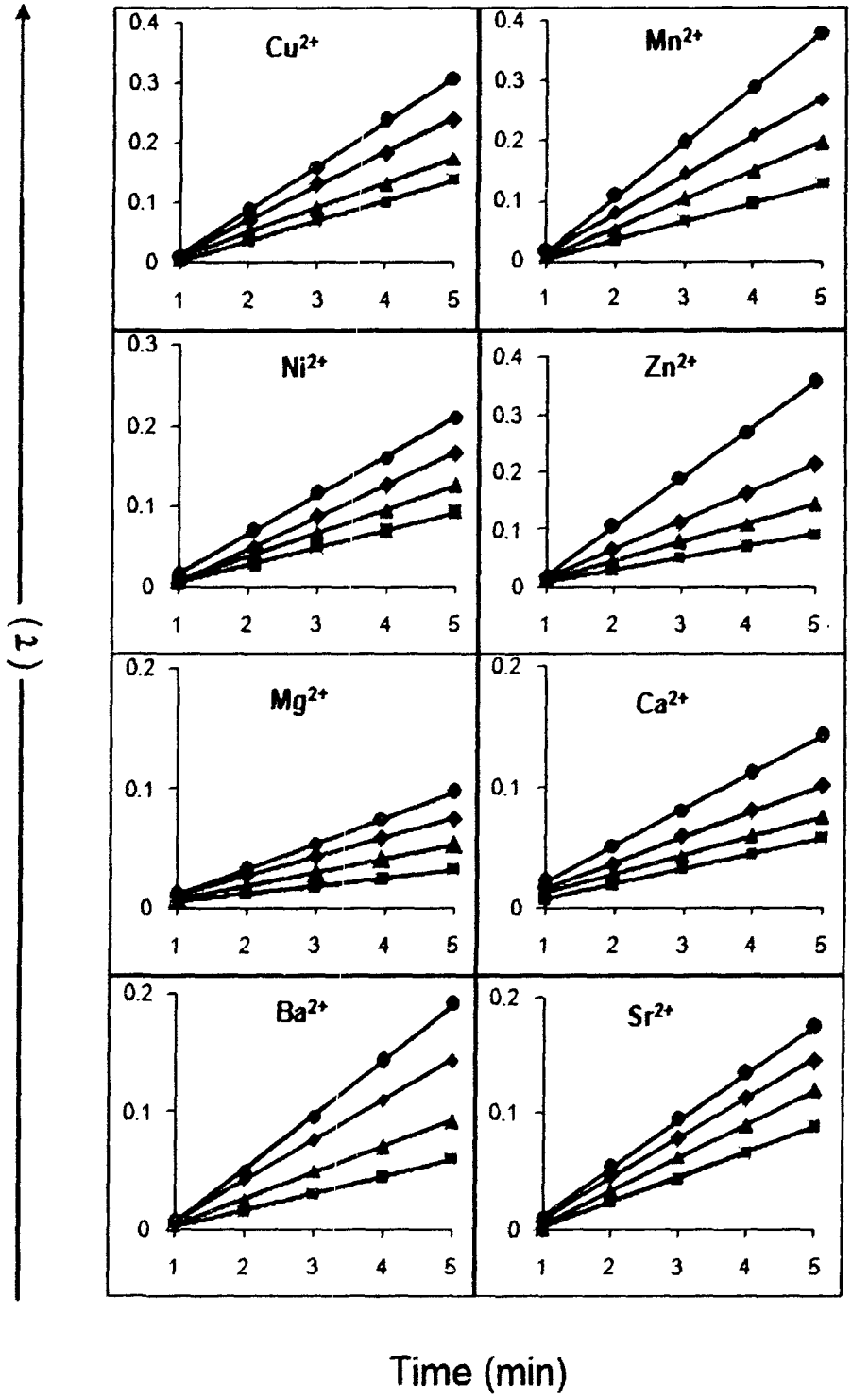


Figure 3.15 Plots of τ vs. *t* (time) for different M(II)–H(I) exchanges at different temperature: (■) 30 °C; (▲) 45 °C; (♦) 60 °C; (●) 75 °C on Nylon-6,6 Sn(IV) phosphate composite cation-exchanger

Table 3.10 Slopes of various τ versus time (t) plots on poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger at different temperatures

Migrating ions	10^2 S (s^{-1})			
	30°C	45°C	60°C	75°C
Mn(II)	3.1	4.9	6.7	9.2
Cu(II)	3.1	4.1	5.8	7.6
Ni(II)	2.1	3.0	4.5	5.4
Zn(II)	2.5	3.3	5.5	8.5
Mg(II)	0.9	1.4	2.1	3.0
Ca(II)	1.1	1.6	2.5	3.5
Ba(II)	1.3	2.1	3.3	4.6
Sr(II)	2.0	2.9	3.5	4.6

Table 3.11 Slopes of various τ versus time (t) plots on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger at different temperatures

Migrating ions	10^2 S (s^{-1})			
	25°C	35°C	50°C	65°C
Mn(II)	4.3	6.2	7.9	9.5
Cu(II)	1.5	2.8	3.7	5.1
Zn(II)	1.8	2.5	3.9	5.7
Ni(II)	1.5	2.1	2.9	3.7
Mg(II)	0.9	1.4	1.9	2.6
Ca(II)	0.8	1.1	1.5	2.0
Ba(II)	1.4	1.8	2.3	3.1
Sr(II)	0.8	1.2	1.5	1.6

Table 3.12 Slopes of various τ versus time (t) plots on Nylon-6,6 Sn(IV) phosphate composite cation-exchanger at different temperature

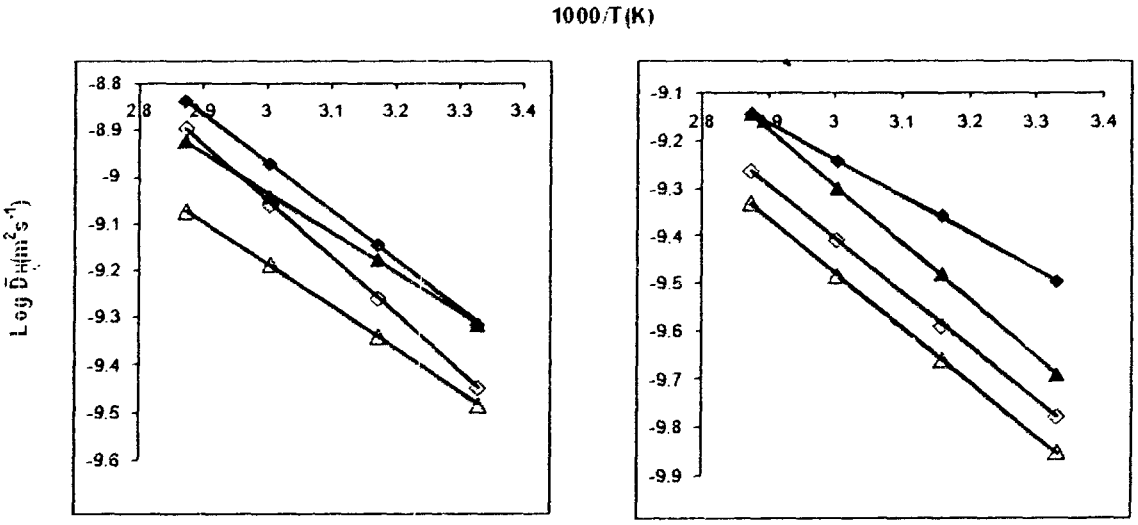
Migrating ions	10^2 S (s^{-1})			
	30°C	45°C	60°C	75°C
Mn(II)	3.0	4.8	6.4	9.1
Cu(II)	3.3	4.1	5.7	7.4
Ni(II)	2.1	2.9	4.0	4.8
Zn(II)	2.0	3.2	4.9	8.4
Mg(II)	0.6	1.1	1.6	2.1
Ca(II)	1.2	1.5	2.1	3.0
Ba(II)	1.4	2.1	3.4	4.5
Sr(II)	2.1	2.9	3.4	4.1

$$\log \bar{D}_{H^+} = D_o \exp(-E_a / RT) \qquad \text{.....3.10}$$

D_0 is obtained by extrapolating these lines and using the intercepts at the origin. The activation energy (E_a) is then calculated with the help of the Eq. 3.10, putting the value of $\bar{D}_{H^+}$ at 273 K. The entropy of activation (ΔS°) were then calculated by substituting D_0 in Eq. 3.11

$$D_o = 2.72 d^2 (kT/h) \exp(\Delta S^\circ / R) \qquad \text{.....3.11}$$

where d is the ionic jump distance taken as 5 A^0 [38], k is the *Boltzmann* constant, R is the gas constant, h is *Plank's* constant and T is taken as 273 K.



(A) **(B)**

Figure 3.16 Plots of $-\log \bar{D}_{H^+}$ vs. $1000/T$ (K) for (A): (■) Mn(II); (▲)Cu(II); (Δ) Ni(II); (□) Zn(II), and (B): (Δ) Mg(II); (□) Ca(II); (▲) Ba(II); (■) Sr(II) on poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger

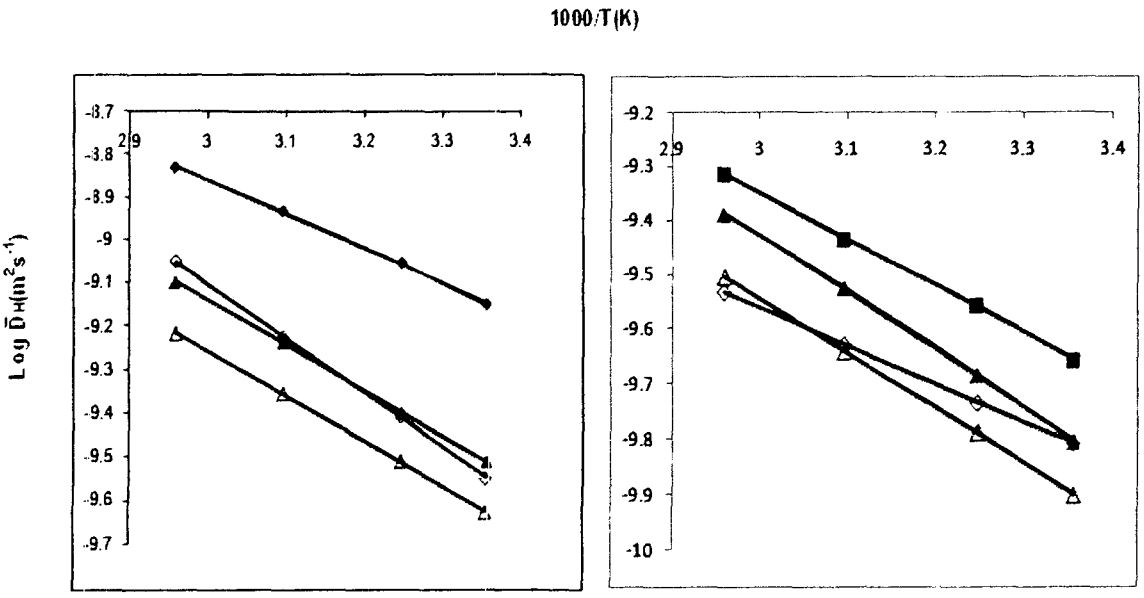


Figure 3.17 Plots of $-\log D_{H^+}$ vs. $1000/T$ (K) for (A): (■) Mn(II); (▲) Cu(II); (Δ) Ni(II); (□) Zn(II), and (B): (□) Mg(II); (■) Ca(II); (Δ) Ba(II); (▲) Sr(II) on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger

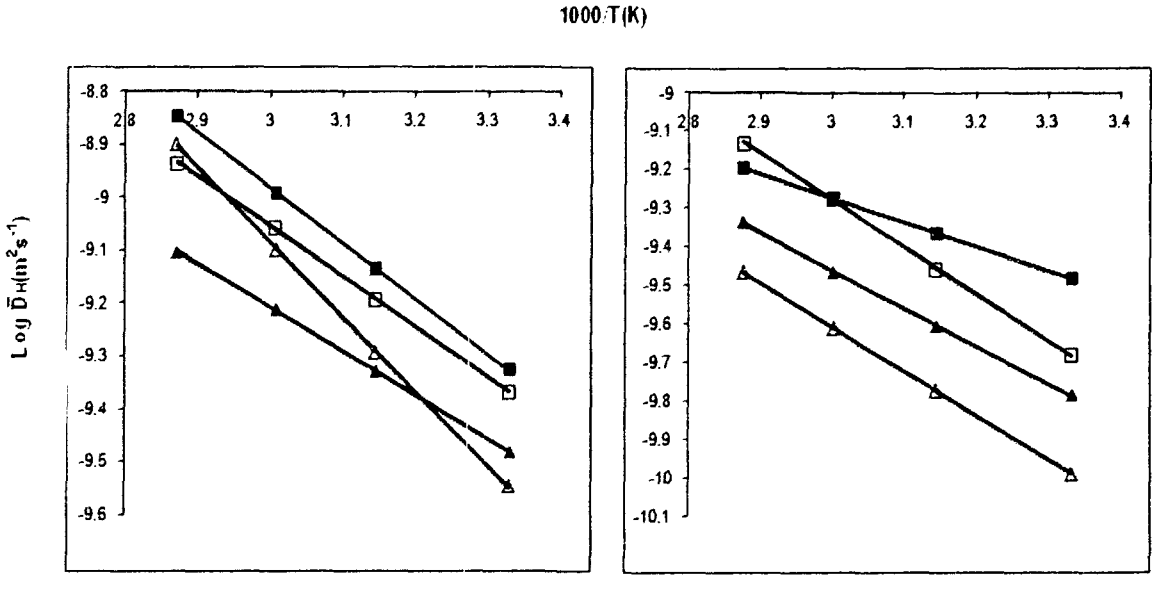


Figure 3.18 Plots of $-\log \bar{D}_{H^+}$ vs. $1000/T$ (K) for (A): (■) Mn(II); (□) Cu(II); (▲) Ni(II); (Δ) Zn(II), and (B): (Δ) Mg(II); (▲) Ca(II); (□) Ba(II); (■) Sr(II) on Nylon-6,6 Sn(IV) phosphate composite cation-exchanger

The values of the diffusion coefficient (D_o), energy of activation (E_a) and entropy of activation ($\Delta S°$), thus obtained are summarized in Table 3.13, Table 3.14 and Table 3.15.

Table 3.13 Values of D_o, Ea and ΔS^0 for the exchange of H(I) with some metal ions on poly-o-toluidine Zr(IV) phosphate nano-composite cation-exchanger

Metal ion exchange with H(I)	10^9 Ionic mobility ($m^2\ V^{-1}\ s^{-1}$)	10^2 ionic radii (nm)	10^7 D_o ($m^2\ s^{-1}$)	Ea (10^2k $Jmol^{-1}$)	ΔS^0 ($J\ K^{-1}\ mol^{-1}$)
Mn(II)	55	9.1	14.75	104.54	0.05
Cu(II)	57	7.0	3.24	84.83	0.16
Ni(II)	52	7.8	3.29	90.09	0.15
Zn(II)	56	8.3	37.03	120.57	0.90
Mg(II)	55	7.8	9.02	114.40	0.29
Ca(II)	62	10.6	9.66	113.01	0.32
Ba(II)	62	12.7	20.11	119.91	0.64
Sr(II)	66	14.3	1.20	77.22	0.59

Table 3.14 Values of D_o, Ea and ΔS^0 for the exchange of H(I) with some metal ions on poly-o-toluidine Ce(IV) phosphate nano-composite cation-exchanger

Metal ion exchange with H(I)	10^9 Ionic mobility ($m^2\ V^{-1}\ s^{-1}$)	10^2 ionic radii (nm)	10^7 D_o ($m^2\ s^{-1}$)	Ea (10^2k $Jmol^{-1}$)	ΔS^0 ($J\ K^{-1}\ mol^{-1}$)
Mn(II)	55	9.1	3.92	81.70	0.075
Cu(II)	57	7.0	10.20	105.0	0.341
Zn(II)	56	8.3	45.19	125.2	0.987
Ni(II)	52	7.8	7.08	103.6	0.182
Mg(II)	55	7.8	5.24	104.9	0.051
Ca(II)	62	10.6	2.82	99.8	0.218
Ba(II)	62	12.7	1.73	86.2	0.430
Sr(II)	66	14.3	0.34	69.6	1.142

Table 3.15 Values of D_0, Ea and ΔS^0 for the exchange of H(I) with some metal ions on Nylon-6,6 Sn(IV) phosphate composite cation-exchanger

Metal ion exchange with H(I)	10^9 Ionic mobility ($m^2 V^{-1} s^{-1}$)	10^2 ionic radii (nm)	10^7 D_0 ($m^2 s^{-1}$)	Ea (10^2k $Jmol^{-1}$)	ΔS^0 ($J K^{-1} mol^{-1}$)
Mn(II)	55	9.1	14.56	104.9	0.50
Cu(II)	57	7.0	6.28	95.1	0.13
Ni(II)	52	7.8	1.89	82.9	0.39
Zn(II)	56	8.3	142.5	141.3	1.49
Mg(II)	55	7.8	6.78	114.6	0.16
Ca(II)	62	10.6	3.08	98.3	0.18
Ba(II)	62	12.7	23.53	121.6	0.70
Sr(II)	66	14.3	0.43	63.5	1.04

The kinetic study reveals that equilibrium is attained faster at a higher temperature (Figure 3.10, Figure 3.11 and Figure 3.12), probably because of a higher diffusion rate of ions through the thermally enlarged interstitial positions of the ion-exchange matrix. The particle diffusion phenomenon is evident from the straight lines passing through the origin for the τ versus time (t) plots, as shown in Figure 3.13, Figure 3.14 and Figure 3.15. Negative values of the entropy of activation suggest a greater degree of order achieved during the forward ion-exchange in M(II)–H(I) process.

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Chapter-4

Electrical Conductivity Measurement Studies on Poly-o-toluidine Zr(IV) Phosphate and Poly-o-toluidine Ce(IV) Phosphate Nano-Composite Cation-Exchange Materials

4.1 Introduction

Research on hybrid organic-inorganic material is an expending area in the materials science [1-10]. Therefore, organic-inorganic composite materials are of intensive interest in the field of contemporary materials chemistry as these materials can exhibit extraordinary properties such as electrical, magnetic and optical properties [11], which arise from the synergism between the properties of the organic and inorganic components. Thus, these materials have gained much interest due to their remarkable change in mechanical [12], thermal [13-16], electrical [17] and magnetic [18] properties compared to pure organic polymers. Additionally, the properties of the composite materials depend on the morphology of the phase's viz. organic and/or inorganic network, which has to be controlled over several length scales. Therefore, the development of such materials is a 'land of multidisciplinarity', where chemists, physicists, material scientists and engineers have to work closely together to fully exploit this technical opportunity for creating materials and device with benefits for the best of two worlds namely inorganic and organic.

One important class of hybrid materials is that in which the inorganic fraction is composed by conducting polymers, in which new inorganic lattice structures are formed, resulting from cooperative interactions between the organic and inorganic components. In all cases, there is promise of developing new materials with properties not seen in purely organic or purely inorganic solids. In general, the formation of hybrids between conducting polymers and inorganic solids aims to obtained composite materials with synergetic or complementary behaviors between the polymer and the inorganic matrices. The properties of the designed composites will depend both on the characteristics of the polymer and on the nature of the inorganic matrices. This approach can be very useful to obtain materials with predominant properties. The electrical conductivity of the conducting polymers is due to the conjugated backbone, which is totally responsible for electroactive character. The electrically conducting polymers are the electro-chromic materials with chemically active surface [19-22]. But they are chemically sensitive and have poor mechanical properties and pose processibility problems. The inherent instability is also due to highly unsaturated backbone of conjugated polymers. Stability problems have, therefore caused many research groups to search for conjugated polymers of high stability. To meet the requirement of stability of materials of improve performance, explosive research is going on to synthesize the composites of 'organic-

organic' and 'organic-inorganic' nature. In the view of the above-mentioned facts, researchers have shown much interest in the study of electrically conducting behavior of 'organic-inorganic' materials [23-30].

In this chapter, we report the preparation of composite of conducting polymers (poly-o-toluidine) and polyvalent metal acid salts [Zr(IV) phosphate and Ce(IV) phosphate] by mixing fixed amounts (vol.%) of organic monomers with different volume of inorganic precipitates while Nylon-6,6 Sn(IV) phosphate is non-conducting composite. The electrical conductivity behavior of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite systems with increasing temperature was measured by using 4-in-line-probe DC electrical conductivity measuring instrument.

4.2 Experimental

4.2.1 Reagents and chemicals

The main reagents used for the synthesis were: Zirconium oxychloride, $ZrOCl_2.8H_2O$ (99%), Cerium sulphate, $Ce(SO_4)_2.4H_2O$ (99% CDH India Ltd.), phosphoric acid, H_3PO_4 (88-93% Loba Chemie India Ltd.), Ammonium persulphate, $(NH_4)_2S_2O_8$ (95% CDH, India), di-sodium hydrogen orthophosphate, Na_2HPO_4 (CDH, India), ortho-toulidine, C_7H_9N (98%, E-Merch India Ltd.), hydrochloric acid HCl, 35% and Nitric acid, HNO_3 (35% E-Merch India Ltd.). All other reagents and chemicals were of analytical reagent grade.

4.2.2 Instrumentation

- A 4-in-line probe electrical conductivity measuring instrument (Scientific Equipment Roorkee, India) was used for measuring DC electrical conductivity.
- A hydraulic pressure instrument was used for making pellets of sample materials.
- An electronic balance (digital) – Sartorius (Japan), model 21 OS.
- A mortar pastel.
- A micrometer having least counts 0.01 mm.

4.2.3 Preparation of the reagent solutions

0.1M solutions of Zirconium oxychloride ($ZrOCl_2.8H_2O$) and tin tetrachloride ($SnCl_4.5H_2O$) were prepared in 4M HNO_3 while ammonium persulphate solution was prepared in 2M HCl. H_3PO_4 solutions of different moralities were prepared in

demineralized (DMW) water and 0.1M $Ce(SO_4)_2.4H_2O$ prepared in 1M H_2SO_4. Solutions of 20% ortho-toluidine of different concentration (v/v) were prepared in 2M HCl.

4.2.4 Preparation of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate nano-composites

Various samples of 'poly-o-toluidine Zr(IV) phosphate' and 'poly-o-toluidine Ce(IV) phosphate' were prepared through the method described in chapter – 2, Section- 2.2.3 by mixing different concentrations of ortho-toluidine into inorganic precipitates of Zr(IV) phosphate and Ce(IV) phosphate, respectively and samples S-5 and T-4 were selected for detailed conductivity studies (Table 2.1 and Table 2.2).

4.2.5 Electrical conductivity measurement studies

The measurements of electrical conductivity were carried out on various samples of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate nano-composites.

4.2.5.1 Treatment with HCl solution (acidic doping)

Poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate nano-composite materials were treated with 0.5M aqueous solution of HCl to induced protonic acid doping. The materials were washed for excess HCl with doubly distilled water repeatedly till the filtrate gave negative test for hydrogen ions. Then the samples were dried at 50 °C in an oven for 48 hours.

4.2.5.2 Sample (pellet) preparation

The dried sample materials were finely ground in a mortar pastel and then taken into a die with spatula. The pellets of different sample materials of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate for electrical conductivity measurement were made at room temperature with the help of a hydraulic pressure instrument, at 25 KN pressure for 20 minute. Thickness of each sample was measured by micrometer at five different points and the average thickness was taken as the thickness of the pellet sample.

4.2.5.3 Instrumental method of electrical conductivity measurements

Four probe DC electrical conductivity measurements with increasing temperature for the representative samples of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV)

phosphate (as prepared and HCI treated) were performed on pressed pellets by using a 4-in-line-probe DC electrical conductivity measuring technique.

The sample to be tested was placed on the base plate of four-probe arrangement and the probes allowed to rest in the middle of the sample. A very gentle pressure was applied on the probes and then it was tightened in this position so as to avoid piercing of the probes into the samples. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of probes was measured. The oven supply was then switched on, the temperature was allowed to increase gradually with current, and voltage was recorded with rise in temperature.

4.2.5.4 Thermal stability of composites in terms of DC electrical conductivity retention

4.2.5.4.1 Isothermal technique

The isothermal stability of the poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite materials in terms of DC electrical conductivity retention were studied under isothermal condition using four-in-line-probe DC electrical conductivity measuring instrument. This study was carried out at 50, 70, 90, 110, 130 and 140 °C for poly-o-toluidine Zr(IV) phosphate at an interval of 15 min while for poly-o-toluidine Ce(IV) phosphate it was carried out at 50, 80, 110 and 150 °C at an interval of 15 min on the selected composite samples (S-5 and T-4, HCI treated).

4.2.5.5 Environmental stability of the conductivity of composites

The stability of the poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite materials (S-5 and T-4, HCI treated) in terms of electrical conductivity retention was studied by repeatedly measuring four-in-line probe DC electrical conductivity at room temperature on pressed pellets at an interval of 10 days by short-term exposure to laboratory air.

4.3 Results and Discussion

In this chapter, various samples of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate electrically conducting 'organic-inorganic' composite materials were chemically prepared by the incorporation of poly-o-toluidine conducting polymers into the inorganic matrices of Zr(IV) phosphate and Ce(IV) phosphate, respectively. Among these, sample S-5 and T-4 (Table 2.1 and Table 2.2 in Chapter 2) were selected for detail electrical conductivity studies.

These composite materials contain two components viz. inorganic and organic. The inorganic components of the composites are the efficient ion-exchange materials whereas organic components, poly-o-toluidine is good electronically conducting polymer. In general, a high electrical conductivity of conductive polymers is attained by dopant, which stabilizes the polaron and bipolaron states as counter anions [31-34].

Thus, the DC electrical conductivity of composite ion-exchange materials is due to the presence of sufficient amount of the conducting polymer and basically it is electronic conduction contributed by the conducting components, i.e. poly-o-toluidine by the charge-transfer reaction between poly-o-toluidine component of the composites and doping agents, HCl, respectively as given:

$$[\text{POTZr(IV)P}] + n\text{HCl} > [\text{POT}\,(n\text{H}^+)\,(n\text{Cl}^-)\,\text{Zr(IV)\,P}] \quad \text{.....4.1}$$

$$[\text{POTCe(IV)P}] + n\text{HCl} > [\text{POT}\,(n\text{H}^+)(n\text{Cl}^-)\,\text{Ce(IV)\,P}] \quad \text{.....4.2}$$

Controlling the doping process (i.e. treatment with aqueous solution of HCl), the electrical conductivity of these materials could be varied from insulator, through semiconductor to metal range and vice-versa. *Schollhorn and Zagefka* [35] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalocogenides, which has further been supported by the work of *Foot and Shaker* [36]. On the basis of the disproportionation reaction of ammonia as suggested by above workers (equation-4.3), *Mohammad* [37] also has suggested an analogous disproportionation reaction for water (Eq. 4.4).

$$8NH_3 > 6NH_4^+ + 6e^- + N_2 \quad \text{.....4.3}$$

$$6H_2O > 4H_3O^+ + 4e^- + N_2 \quad \text{.....4.4}$$

The basic strength of water is very low, hence does not act as undoping agent in case of poly-o-toluidine. However, the neutralization reactions to undope poly-o-toluidine within poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite cation-exchange materials may be carried out by ammonia.

4.3.1 Electrical conductivity measurements

Electrical conductivities of the pellets of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite samples were determined from the measurement of conductivity of the samples using the four-probe method of conductivity measurement for semiconductors. That is the most satisfactory method as it overcomes difficulties, which are encountered in conventional methods of conductivity measurement (i.e; two probes), e.g. the rectifying nature of metal semiconductor contacts and the injection of minority carriers by one of the current carrying contacts, which affects the potential of other contacts and modulate the conductance of the material etc. It also permits, measurement of conductivity in sample having wide variety of shapes. In order to use the four-probe method it is necessary to make the following assumptions:

- The conductivity of the material is uniform within the area of measurements. If there is minority carrier injection into the material to be tested by the current carrying electrodes, most of the carriers recombine near the electrodes so that their effect on the conductivity is negligible.
- The surface on which the probe rest is flat with no surface leakage.
- The four-probe used for conducting measurement must contact the surface at point that lie in straight line.
- The diameter of the contact between the metallic probes and the material should be smaller than the distance between the probes.
- The surface of the materials may be conducting or non-conducting.
- A conducting boundary is one in which the bottom surface of the material to be tested is of much higher conductivity than that of the material itself. This could be achieved by copper plating on the bottom surface of the semiconductor slice.
- A non-conducting boundary is produced when the bottom surface of the material to be tested is in contact with an insulator such as poly-tetrafluoroethylene in these measurements.

After the measurements of current-voltage data by a four-in-line probe DC electrical conductivity measuring instrument was processed for calculation by using the following Equataion-

$$\rho = \rho_0 / G_7 (W / S) \quad \text{.....4.5}$$

where ρ is corrected resistivity (ohm cm), ρ_0 = uncorrected resistivity (ohm cm), $G_7(W/S)$ is the correction factor used for the case of a non conducting bottom surface, which is a function of W, the thickness of the sample under test (cm) and S, the probe spacing (cm); i.e.

$$G_7 (W / S) = (2S / W) \ln 2 \quad \text{..... 4.6}$$

$$\rho_0 = V / I \times 2\pi S, \quad \text{.....4.7}$$

$$\sigma = \frac{1}{\rho} \quad \text{.....4.8}$$

where I is the current (A), V is the voltage (V) and σ = DC electrical conductivity (S cm^{-1}). Although the electrical conductivity measurements were done under ambient conditions, the composite samples were thoroughly dried before making the pellets and performing the electrical conductivity measurements. Hence, the contribution of protonic conductivity to the total electrical conductivity due to the presence of moisture should be minimum and need not to be taken into consideration.

Poly-o-toluidine Zr(IV) phosphate composite material was treated with 0.5M NaCl, KCl, $ZnCl_2$, $Pb(NO_3)_2$, $MgCl_2$ and $Cu(NO_3)_2$ solutions, and electrical conductivity measurements were carried out on these different forms (Na^+, K^+, Zn^{2+}, Pb^{2+}, Mg^{2+}, Cu^{2+}) of composite cation-exchange material.

The variations of electrical conductivity (σ) of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite samples (as prepared and HCl treated), prepared with 20% ortho-toluidine with increasing temperature (between 30 °C to 200 °C) were carried out. On examination, it was observed that the electrical conductivity of the composite samples increase with the increase in temperature and the values lie in the order of 10^{-2} to 10^{-3} S/cm for both poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate i.e; in the semiconductor region. To determine the nature of dependence of electrical conductivity on temperature plots of *log* σ versus *1000 / T(K)* were drawn (Figure 4.1 and Figure 4.2) and they followed *Arrhenius* equation similar to other semiconductors [38].

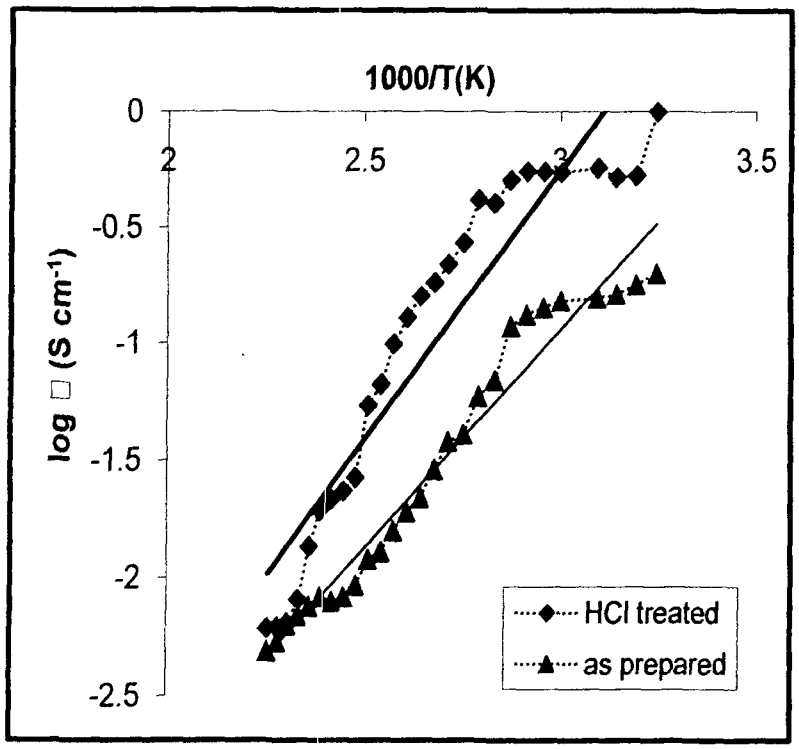

Figure 4.1 Arrhenius plots for poly-o-toluidine Zr(IV) phosphate nano-composite material

It was also observed that the composite materials showed enhanced electrical conductivity on exposure to HCl as compared to original form, due to the charge- transfer reaction between poly-o-toluidine component of the composites and doping agents, HCl as described above. The dependence of the electrical conductivity through the bi-phasic systems poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composites (prepared with 20% concentrations of ortho-toluidine) on the concentration of conducting phases (i.e. poly-o-toluidine) was examined.

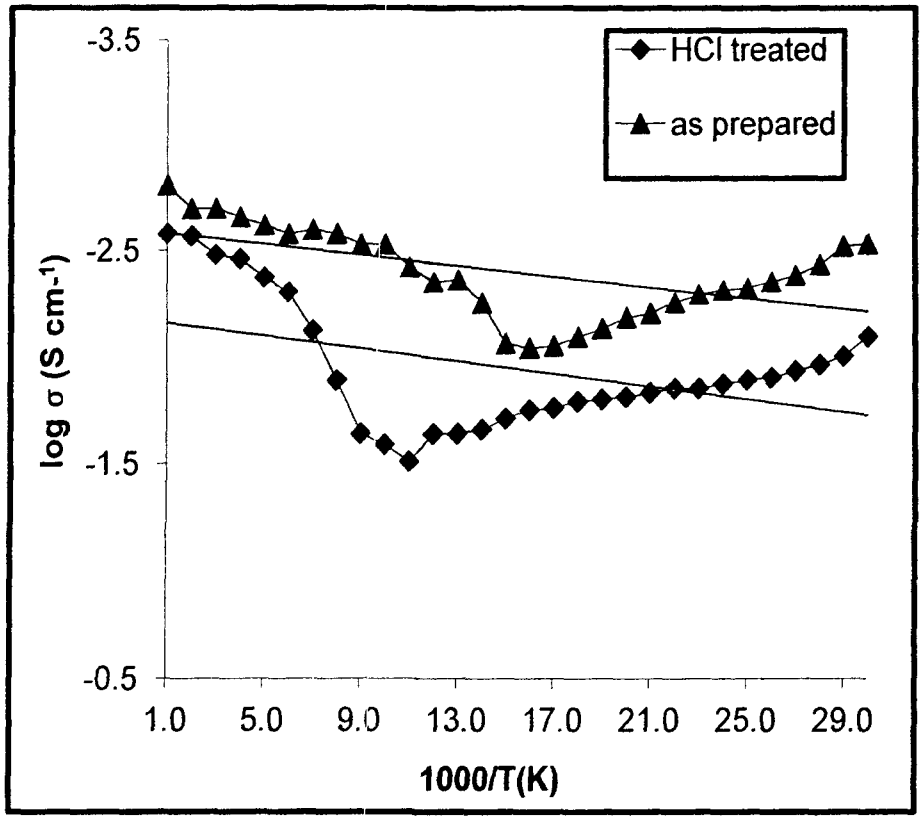

Figure 4.2 Arrhenius plots for poly-o-toluidine Ce(IV) phosphate nano-composite material

Thus, we can say that main factor that made the composites electrically conductive is the presence of poly-o-toluidine in sufficient amount. Thus, major part of electrical conductivity of the composite is due to the incorporation of poly-o-toluidine in the composites.

Poly-o-toluidine Zr(IV) phosphate nano-composite material was also treated with 1M NaCl, $ZnCl_2$, $Pb(NO_3)_2$, KCl, $MgCl_2$ and $Cu(NO_3)_2$ solutions, and electrical conductivity measurements were carried out on these different forms (Na^+, Zn^{2+}, K^+, Pb^{2+}, Mg^{2+}, Cu^{2+}) of material. It was observed that the sample S-5 treated with $Pb(NO_3)_2$ showed the higher electrical conductivity while treated with KCl and $Cu(NO_3)_2$ showed lower electrical conductivity at room temperature as given in Table 4.1.

Table 4.1 Four-probe DC electrical conductivity of different forms of poly-o-toluidine Zr(IV) phosphate composite system at ambient temperature (prepared with 20% o-toluidine monomers)

Sample No.	Poly-o-toluidine Zr(IV) phosphate nano-composite	Conductivity (S cm^{-1})
1.	As prepared	1.08×10^{-2}
2.	HCl treated	1.37×10^{-3}
3.	NaCl treated	1.83×10^{-2}
4.	$ZnCl_2$ treated	1.72×10^{-2}
5.	KCl treated	8.10×10^{-4}
6.	$Pb(NO_3)_2$ treated	4.19×10^{-2}
7.	$MgCl_2$ treated	1.21×10^{-2}
8.	$Cu(NO_3)_2$treated	1.66×10^{-3}

4.3.2 Stability of composites in terms of DC electrical conductivity retention

The thermal stability of the poly-o-toluidine Zr(IV) phosphate (S-5) and poly-o-toluidine Ce(IV) phosphate (T-4) composite materials (HCl treated) in terms of DC electrical conductivity retention was studied under isothermal condition at 50, 70, 90, 110, 130 and 150 °C for poly-o-toluidine Zr(IV) phosphate while at 50, 80, 110 and 150 °C for poly-o-toluidine Ce(IV) phosphate measuring four-in-line- probe DC electrical conductivity at an interval of 15 minutes. The electrical conductivity measured with respect to the time of accelerated ageing is presented in Figure 4.3 and Figure 4.4.

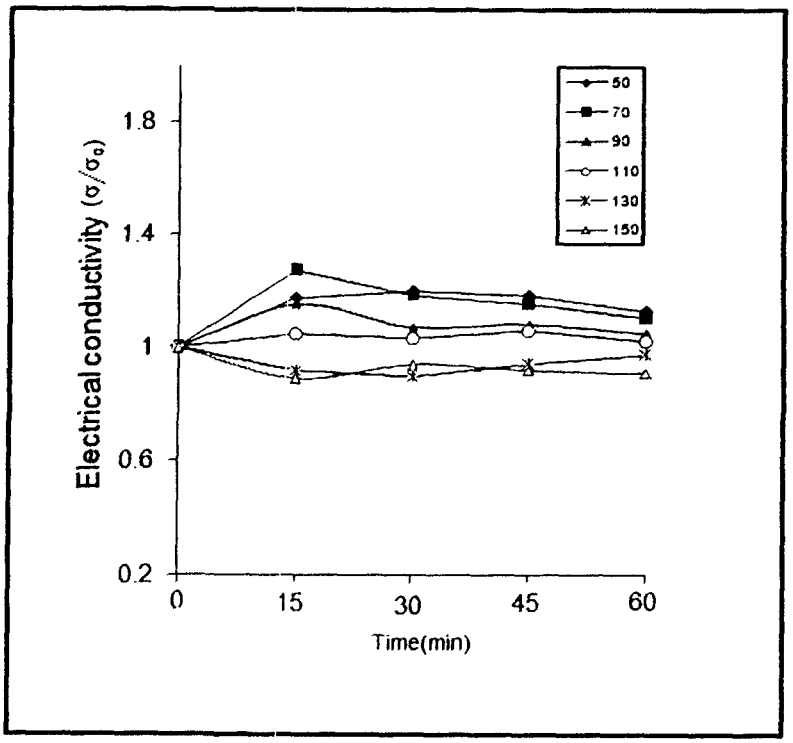

Figure 4.3 Isothermal stability of poly-o-toluidine Zr(IV) phosphate nano-composite in terms of DC electrical conductivity with respect to time at 50, 70, 90, 110, 130 and 150°C

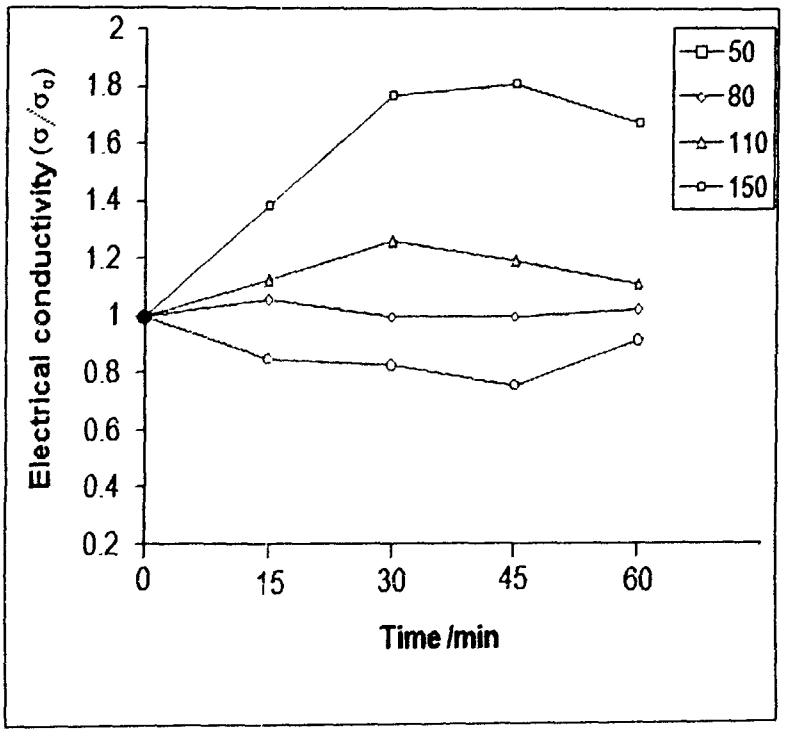

Figure 4.4 Isothermal stability of poly-o-toluidine Ce(IV) phosphate composite in terms of DC electrical conductivity with respect to time at 50, 80 , 110 and 150 °C

It was observed that the electrical conductivity is quite stable at 50, 70, 90 and 110 °C that supports the fact that the DC electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 and 150 °C for poly-o-toluidine Zr(IV) phosphate and decreases with time at 110 and 150 °C for poly-o-toluidine Ce(IV) phosphate that may be attributed to the loss of dopant and chemical reaction of dopant with the material.

These composite materials were also observed to be a stable materials, i.e; the room temperature conductivity is negligibly affected by short- term exposure to laboratory air as evident from Figure 4.5 and Figure 4.6. The materials of these types may often exhibit increase in conductivity upon short-term exposure to oxygen, which is attributed to the formation of a charge transfer complex with oxygen and may involve O^{2-} . Presumably, electron transfer from the polymer chain. Thus, short-term exposure to oxygen may increase the conductivity of the material by increasing the concentration of charge carriers. Oxygen can also produce a decrease in the conductivity of the material through a destructive reaction, e.g; exposure of the composite to oxygen results in a decrease in the conductivity due to an irreversible reaction that is believed to generate covalently bonded oxygen species. Axially bound water is also responsible for part of the conductivity loss during the ageing of the material.

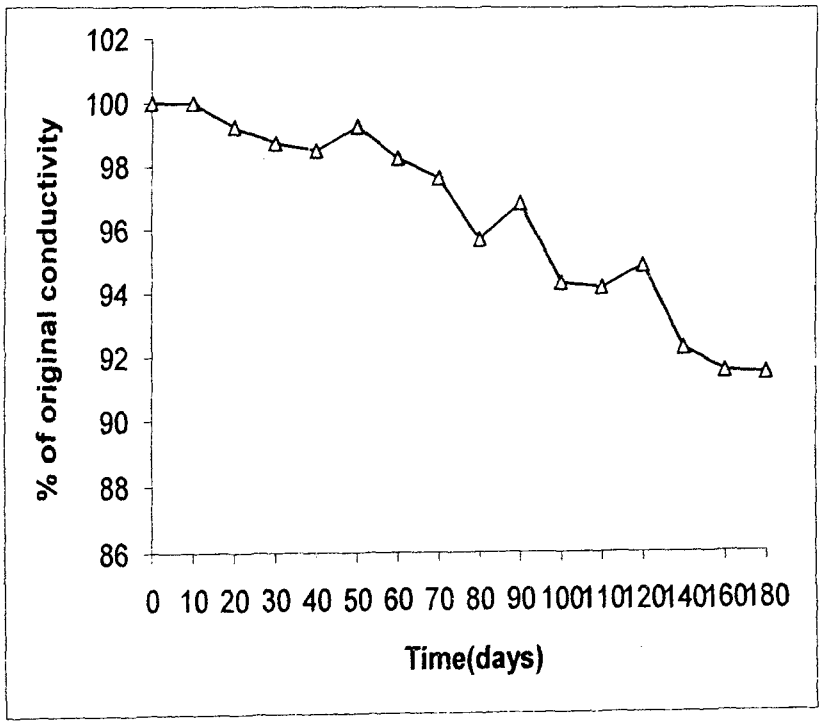

Figure 4.5 Conductivity verses time on exposure to laboratory air for poly-o-toluidine Zr(IV) phosphate nano-composite material (HCl treated)

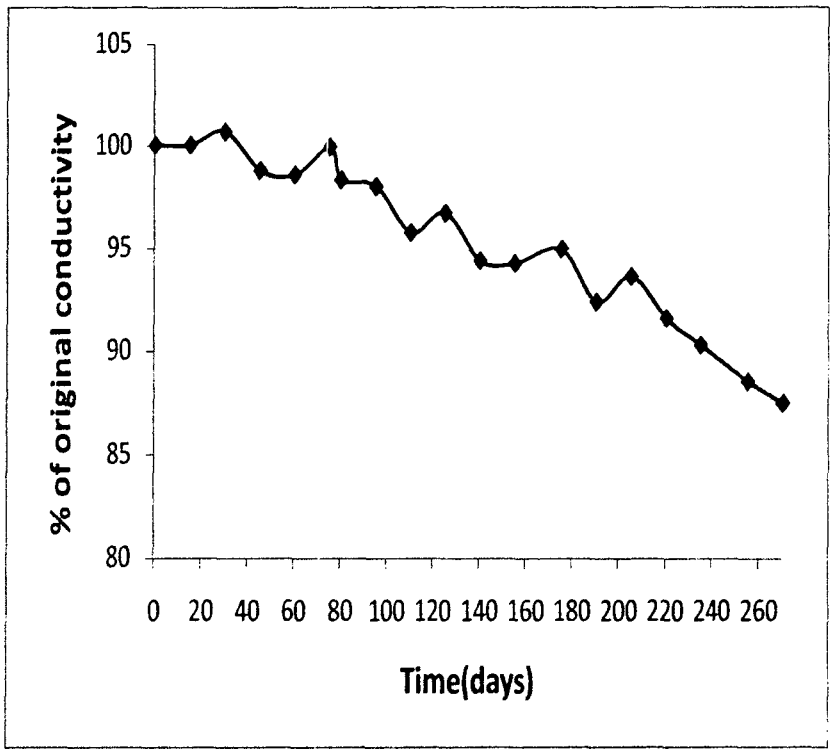

Figure 4.6 Conductivity versus time of exposure to laboratory air for poly-o-toluidine Ce(IV) phosphate composite material (HCl treated)

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Chapter-5

Preparation and Characterization of Composite Cation-Exchanger Membrane and their Applications in making Ion-Selective Membrane Electrode Using: Poly-o-toluidine Zr(IV) phosphate, Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate

5.1 Introduction

The increasing demand for chemical surveillance in environment protection, medicine and many industrial processes has created the need for sensors with features such high selectivity, sensitivity, reliability and sturdiness. These demand can often be satisfied by ion-selective electrodes (ISEs), which are commonly used owing to their simplicity, lower cost, fast provision for analytical results and high selectivity for heavy toxic metal ions [1,2]. Therefore, ion-selective electrodes are important analytical tools allowing the sensitive and selective determination of various ions in the wide range of concentration [3]. Precipitate based ion selective membrane electrodes are well known as they are successfully employed for the determination of several anions and cations [4]. There are some homogeneous as well as heterogeneous hybrid ion-exchange membranes. Homogenous ion-exchange membranes are coherent ion-exchanger gels in the shape of disks, ribbons etc. The heterogeneous precipitate ion-exchange membranes consist of suitable colloidal ion-exchanger particles as electroactive materials embedded in polymer (binder), poly (vinyl chloride) (PVC) or epoxy resin (Araldite) or polystyrene, polyethylene, nylon etc., by physical mixing or chemical reaction and have been extensively studied as potentiometer sensors [5-11]. Therefore, ion-exchange membrane also finds application in diverse processes such as (electrodialysis, diffusion dialysis, electro-deionization, membrane electrolysis, fuel cells, storage batteries, electro-chemical synthesis etc), which are energy source and environmental saving.

Now a days, the use of organic–inorganic composite ion-exchange materials formed by the combination of inorganic precipitate and organic polymer as electroactive components in membrane electrodes has generated widespread interest in developing new ion selective electrodes using as sensors for sensor applications [12-15], especially for the determination of heavy toxic metals [16,17]. Therefore, we also made an effort to develop new and novel composite cation-exchange material through incorporating of electrically conducting organic polymer into the matrices of inorganic precipitate of multivalent metal acid salt that are attractive for the purpose of creating high performance of high functional polymeric material with good electrochemical properties. The research work was carried out to obtain new heterogeneous precipitate based membrane ion-selective electrodes using poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite as electro-active phase for the determination of Hg(II) and Cd(II) ions present in the solution. This chapter represents the preparation,

characterization and fabrication of ion-exchange membrane and ion-selective membrane electrode based on the aforesaid composite materials.

5.2 Experimental

5.2.1 Reagents and instruments

The main reagents used for the synthesis of the materials were obtained from CDH, Loba Chemie, E-merck and Qualigens (India Ltd., used as received), PVC (Ciba-Geigy, India Ltd.) and Araldite. All other reagents and chemicals were of analytical grade.

A digital pH – meter (Elico Li-10, India), double beam atomic absorption spectrophotometer (GBC 902, Australia), a digital potentiometer (Equiptronics EQ 609, India); accuracy ±0.1mV with a saturated calomel electrode as reference electrode, an electronic balance (digital) –(Sartorius 21OS, Japan) and an agate mortar pastel were used.

The stock solution of 1×10^{-1} M Hg(II) and Cd(II) were prepared in double distilled water (DMW). The solution was standardized by complexometric titration [18]. The working standard solutions (1×10^{-1} M to 1×10^{-10} M) were prepared by proper dilution of the stock solution.

5.2.2 Preparation of electroactive phase: poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchangers

A number of samples of 'poly-o-toluidine Zr(IV) phosphate', 'poly-o-toluidine Ce(IV) phosphate' and 'Nylon-6,6 Sn(IV) phosphate' composite cation-exchange materials were prepared as described in Chepter-2 (Section 2.2.3). The sample S-5 (Table 2.1), sample T-4 (Table 2.2) and sample P-4 (Table 2.3) were chosen as electroactive phase for the potentiometric studies.

5.2.3 Preparation of ion-exchange membranes

The ion-exchange membranes were prepared by employing an electroactive ion-exchange material into a polymer binder (Polyvinyl Choliride or Araldite). For this, electroactive component poly-o-toluidine Zr(IV) phosphate (S-5), poly-o-toluidine Ce(IV) phosphate (T-4) and Nylon-6,6 Sn(IV) phosphate (P-4) materials were taken to be embedded in polyvinyl chloride (PVC) and Araldite.

5.2.4 Preparation of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate membrane

For the preparation of ion-exchange membrane, *Coetzee and benson* [19] procedure was employed. Poly-o-toluidine Zr(IV) phosphate cation-exchanger was grinded to fine powder and was mixed thoroughly with polyvinyl chloride (PVC), dissolved in 10 ml of tetrahydrofuran (THF), and finally mixed with 10 drops of dioctylthalate used as plasticisizer [20]. The mixing ratio of the ion-exchanger was varied with a fixed content of PVC in order to obtain a composition, which gave the membrane showing the best performance and the resulting solutions were carefully poured into a glass casting ring (diameter 10 mm) resting on a glass plate. These rings were left for slow evaporation of THF to obtain thin films. In this way, three films of cation exchanger, poly-o-toluidine Zr(IV) phosphate with different thickness of master membrane were prepared as given in Table 5.1.

Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate cation-exchangers as electroactive material were ground to fine powder and was mixed thoroughly with Araldite (Ciba-Geigy, India Ltd.) in 1:1 (w/w) ratio to make a homogeneous paste, which was then spread between the folds of Whatman's filter paper No. 42. Glass plates were kept below and above the filter paper folds as support. The phase of the exchanger and Araldite was kept under pressure of 2 kg cm^2 for 24 h and left to dry. Two sheets of different thickness of master membranes were prepared. These sheets were dipped in distilled water to remove filter paper. After drying, the membrane sheets as given in Table 5.2 and Table 5.3 were cut in the shapes of discs using a sharp edge blade.

5.3 Characterization of Membranes

The pre-requisite performance of an ion-exchanger membrane is its complete physicochemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. Thus some parameters such as porosity, water content, swelling, thickness, etc. were determined as described elsewhere [21-24].

Table 5.1 Characterization of poly-o-toluidine Zr(IV) phosphate composite cation-exchange membrane

Sample	Membrane composition			Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
	Poly-o-toluidine Zr(IV) phosphate (mg)	PVC (mg)	Plasticizer (drops)				
M-1	100	200	10	0.14	1.89	0.200	0.1
M-2	200	200	10	0.20	2.27	0.214	0.2
M-3	400	200	10	0.32	3.89	0.244	0.4

Table 5.2 Characterization of poly-o-toluidine Ce(IV) phosphate composite cation-exchange membrane

Sample No.	Ratio of Poly-o-toluidine Ce(IV) phosphate with Araldite	Thickness of the membrane (mm)	Water content as % weight of wet membrane	Porosity	Swelling of % weight of wet membrane
M-1	2:2	0.24	6.38	7.423×10^{-3}	No swelling
M-2	1:1	0.19	7.52	6.964×10^{-3}	No swelling

Table 5.3 Characterization of Nylon-6,6 Sn(IV) phosphate composite cation-exchange membrane

Sample No.	Ratio of Nylon-6,6 Sn(IV) phosphate with Araldite	Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
M-3	1:1	0.16	1.06	0.210	swelling
M-4	2:2	0.20	2.12	0.244	swelling

5.3.1 Conditioning of the membranes

The membranes were conditioned by equilibrating with 1M sodium chloride; about 1 ml of sodium acetate was also added to adjust the pH 5.0-6.5 (to neutralize the acid present in the films).

5.3.2 Water content (% total wet weight)

First the membranes were soaked in water to elute diffusible salt, blotted quickly with *Whatmann* filter paper to remove surface moisture and immediately weighted. These were further dried to a constant weight in a vacuum over P_2O_5 for 24 h. The water content (total wet weight) was calculated as:

$$\% \text{ Total wet weight} = \frac{W_w - W_d}{W_w} \times 100 \qquad \text{.....5.1}$$

where W_d = weight of the dry membrane and W_w = weight of the soaked/wet membrane.

5.3.3 Porosity

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data:

$$\varepsilon = \frac{W_w - W_d}{A \; L \; \rho_w} \qquad \text{.....5.2}$$

where W_w = weight of the soaked/wet membrane, W_d = weight of the dry membrane, A = area of the membrane, L = thickness of the membrane and ρ_w = density of water.

5.3.4 Thickness and swelling

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze. Swelling is measured as the difference between the average thicknesses of the membrane equilibrated with 1M NaCl for 24h and the dry membrane.

5.3.5 Fabrication of ion-selective membrane electrode

The membrane sheets of poly-o-toluidine Zr(IV) phosphate (0.14 mm thickness), poly-o-toluidine Ce(IV) phosphate (0.19 mm thickness) and Nylon-6,6 Sn(IV) phosphate (0.16 mm thickness) as obtained by the above procedure were cut in the shape of disc and

mounted at the lower end of a Pyrex glass tube (o.d. 0.8 cm, i.d. 0.6 cm) with araldite. Finally the assembly was allowed to dry in air for 24 h. The glass tube was filled with solution of the ion (as reference) towards which the membrane is selective and keep dipped in an identical solution of the same ion at room temperature. In case of poly-o-toluidine Zr(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite ion-selective membrane electrodes, the glass tube was filled with 0.1M mercuric nitrate while in case of poly-o-toluidine Ce(IV) phosphate, the glass tube was filled with 0.1M cadmium nitrate solution respectively. Saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as external reference electrode. The whole arrangement can be shown as:

Internal reference electrode (SCE) Hg, Hg_2Cl_2(s) KCl (satd)	Internal electrolyte (0.1 M Hg^{2+})	Membrane	Sample solution	External reference electrode (SCE) Hg, Hg_2Cl_2(s) KCl (satd)
		And		
Internal reference electrode (SCE) Cd, $CdCl_2$(s) KCl (satd)	Internal electrolyte (0.1 M Cd^{2+})	Membrane	Sample solution	External reference electrode (SCE) Cd, $CdCl_2$(s)KCl (satd)

5.4 Characterization of Ion-Selective Membrane Electrode

In order to study the characteristics of the electrodes, the following parameters were evaluated: lower detection limit, electrode response curve, response time, working pH range and selectivity.

5.4.1 Electrode response or membrane potential

To determine the electrode response, a series of standard solutions to be studied of varying concentrations were prepared. External electrode and ion-selective membrane electrode are plugged in digital potentiometer and the potentials were recorded. The response of the electrodes in terms of the electrode potential (at 25 ±2 °C), corresponding to the concentration of a series of standard solutions of $Hg(NO_3)_2$ and $Cd(NO_3)_2$ in the range (1×10^{-10} - 1×10^{-1} M) were determined at a constant ionic strength as described by IUPAC Commission for Analytical Nomenclature [25]. A calibration curve was made by measuring the electrode response to standard solutions prepared by serial dilution without the addition of extra indifferent salts. The ionic strength will increased linearly with an

increase concentration. This will lead to a gradual decrease of the activity coefficient and the calibration curve [E versus log (concentration)] showed a negative deviation from the straight line for concentration above10^{-3} to 10^{-2} M. This curvature of the calibration curve can be precluded by working at constant ionic strength. This is commonly achieved by adding a large excess of an indifferent electrolyte, the ionic strength buffer. The membrane electrodes were conditioned by soaking: In 0.1M $Hg(No_3)_2$ solution for 5-7 days and for 1 hour at least before use for the poly-o-toluidine Zr(IV) phosphate and Nylon-6,6 Sn(IV) phosphate ion-selective membrane electrodes.

In 0.1M $Cd(NO_3)_2$ solution for 5-7 days and for 1 h at least before use for the poly-o-toluidine Ce(IV) phosphate ion-selective membrane electrode.

The experiments were conducted in air thermostat maintained at 25 ± 1 °C, after performing the experiments, membrane electrode were removed from the test solution and kept in 0.1M selective metal ion solution. Potential measurements of the membrane electrode were plotted against the selected concentrations of the respective ions in aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system.

5.4.2 Effect of pH

A series of pH solution ranging from 1-13 were prepared at constant ion concentration i.e (1×10^{-3} M) for poly-o-toluidine Zr(IV) phosphate; (1×10^{-2} M) for poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate electrodes. The pH variations were brought out by the addition of dilute acid (HCl) and dilute base (NaOH) solutions. The values of electrode potential for the electrodes at each pH were recorded (Table 5.4) and were plotted against pH.

5.4.3 Response time

The response time was measured by recording the EMF of the electrodes as a function of time when it was immersed in the solution to be studied. The method of determining response time in the present work is being outlined as follows:

The electrode is first dipped in 1×10^{-3} M solution of the ion concerned and immediately shifted to another solution (pH~4) of 1×10^{-2} M ion concentration of the same ion (10 fold higher concentration). The potential of the solution was read at zero second that is, just after dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 s. The potentials were then plotted vs. the time. The time

during which the potentials attain a constant value represent the response time of the electrode (Table 5.5).

Table 5.4 Effect of pH on electrode response of Hg^{2+} and Cd^{2+} ion selective poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate membrane electrode

pH ↓ Membrane electrodes→	Measured electrode potential		
	Poly-o-toluidine Zr(IV) phosphate (-mV)	Poly-o-toluidine Ce(IV) phosphate (-mV)	Nylon-6,6 Sn(IV) phosphate (-mV)
1	256	300	176
2	240	248	248
3	241	384	354
4	241	390	380
5	242	390	380
6	241	389	379
7	241	389	377
8	243	296	296
9	280	238	234
10	293	218	216
11	298	198	198
12	310	180	180
13	312	180	174

Table 5.5 Response of Hg^{2+} and Cd^{2+} ion selective membrane electrodes of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate at different time intervals (at 1×10^{-2} M)

Time sec ↓ Membrane electrodes →	Measured electrode potential		
	Poly-o-toluidine Zr(IV) phosphate (-mV)	Poly-o-toluidine Ce(IV) phosphate (-mV)	Nylon-6,6 Sn(IV) phosphate (-mV)
00	322	340	522.83
05	315	340	522.83
10	315	348	523
15	315	349	523
20	315	351	524
25	315	351	524
30	316	351	524.8
35	316	351	524.8
40	316	351	526
45	316	-	526
50	-	-	526
55	-	-	526

5.4.4 Selectivity coefficients

To study the cationic interference due to other ions, the selectivity coefficients of various interferring cations for poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate ion-selective membrane electrodes were determined by the mixed solution method as described elsewhere [26]. The method is discussed below:

A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-2} M) and varying concentrations (1×10^{-1} to 1×10^{-10}) of the primary ion. Now the potential measurements were made by using the membrane electrode assembly (Table 5.6).

Table 5.6 Selectivity coefficient values for Hg^{2+} and Cd^{2+} selective poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate membrane electrode

S.No.	Poly-o-toluidine Zr(IV) phosphate		Poly-o-toluidine Ce(IV) phosphate		Nylon-6,6 Sn(IV) phosphate	
	Interfering ions (M^{n+})	Selectivity coefficient values	Interfering ions (M^{n+})	Selectivity coefficient values	Interfering ions (M^{n+})	Selectivity coefficient values
1	Pb^{2+}	1×10^{-1}	Zn^{2+}	0.069	Zn^{2+}	0.025
2	Cr^{3+}	1×10^{-2}	Ni^{2+}	0.007	Cd^{2+}	0.055
3	Fe^{3+}	1×10^{-2}	Cu^{2+}	0.076	Cu^{2+}	0.040
4	Zn^{2+}	5×10^{-2}	Ca^{2+}	0.076	Mg^{2+}	0.035
5	Co^{2+}	5×10^{-2}	Hg^{2+}	0.059	Co^{2+}	0.020
6	Cd^{2+}	5×10^{-2}	Pb^{2+}	0.080	Na^{+}	0.005
7	Ba^{2+}	1×10^{-2}	Cr^{2+}	0.006	K^{+}	0.9500
8	Al^{3+}	1×10^{-3}	Ba^{2+}	0.089	Fe^{2+}	0.400
9	Na^{+}	5.5×10^{-3}	Hg^{2+}	0.900	Sr^{2+}	0.910
10	K^{+}	5.5×10^{-3}	Sr^{2+}	0.810	Pb^{2+}	0.900
11	Mg^{2+}	5.5×10^{-3}	-	-	-	-
12	Ca^{2+}	5.45×10^{-3}	-	-	-	-
13	Sr^{2+}	5.45×10^{-3}	-	-	-	-

5.4.5 Life span of the membrane

In order to find out the life time of electrode, the electrode responses were noted for one or more weeks over weak and response curve is drawn for the data. The electrode response curve showed that the response remains constant over a period of time. After this period the electrode starts behaving irregular, therefore cannot be used for any

measurements. This period in which the electrode response is constant can be termed as life of electrode.

5.5 Results and Discussion

In this chapter, organic-inorganic composite cation-exchangers poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate were used as electroactive material embedded in inert polymer binder (PVC or Araldite) for the preparation of heterogeneous ion-selective membrane electrodes.

5.5.1 Characterization of composite cation-exchanger membranes

Sensitivity and selectivity of the ion-selective membrane electrodes depend upon the nature of electroactive material, membrane composition and physico-chemical properties of the membranes employed. A number of samples of the poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite membranes were prepared with different amount of composite with fixed amount of PVC or Araldite and checked for the mechanical stability, surface uniformity, materials distribution, cracks and thickness etc.

It is necessary to have a preliminary investigation with the membrane that must exhibit some promising selectivity for particular metal ions. Thus, the results of thickness, swelling, porosity and water content capacity of the poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchanger membrane are investigated to find out one membrane of good electrochemical performance for the purpose of preparation of ion-selective electrode and the results are summarized in Table 5.1, Table 5.2 and Table 5.3 respectively. The membrane sample M-1 (thickness 0.14 mm) for poly-o-toluidine Zr(IV) phosphate, M-2 (thickness 0.19) for poly-o-toluidine Ce(IV) phosphate and M-3 (thickness 0.16) for Nylon-6,6 Sn(IV) phosphate composite were selected for further studies.

5.5.2 Potentiometric studies of heterogeneous poly-o-toluidine Zr(IV) phosphate nano-composite membrane electrode

Poly-o-toluidine Zr(IV) phosphate nano-composite membrane (M-1) was fabricated into ion-selective electrode and the membrane electrode was placed in 0.1M $Hg(NO_3)_2$ solution for 7 days to get it conditioned. After conditioning the electrode, the potentials for a series of standard solution of the $Hg(NO_3)_2$ in the range 10^{-10} M to 10^{-1} M were

measured at a fixed concentration of Hg^{2+} ion as internal reference solution. The choice of Hg^{2+} ions depends on its distribution behavior patterns.

After conditioning of the electrode, the potentials for a series of standard solution of the $Hg(NO_3)_2$ in the range 10^{-10} M to 10^{-1} M were measured, maintaining a fixed concentration of Hg^{2+} ion as internal reference solution. It was observed that the most favorable concentration of reference solution, for smooth functioning of the proposed membrane sensor is 0.1M.

Potential measurements of the heterogeneous precipitate based membrane electrodes were plotted against the selected concentration of the Hg^{2+}ions (Figure 5.1) and gives linear response in the range 1×10^{-1} M - 1×10^{-6} M. The limit of detection determined from the intersection of the two extrapolated segments of the calibration graph [27] was found to be 1×10^{-6} M, and thus the working concentration range is found to be 1×10^{-1} M to 1×10^{-6} M for Hg^{2+} ions with a *Nerstian* slope of 30 mV per decade change in Hg^{2+} ion concentration, the slope value is close to *Nerstian* value 29.6 ±3 mV per concentration decade for divalent cation. Below 1×10^{-6} M non-linear response was observed that could be used for analytical applications [28].

In order to investigate pH effect on the potential response of the electrode, the potential were measured for a fixed concentration of Hg^{2+} ions in different pH values. The measurements were carried out at different concentrations (1×10^{-2} M and 1×10^{-3} M) of Hg^{2+} ion solutions but the results were recorded only for 1×10^{-2} M ion solutions.

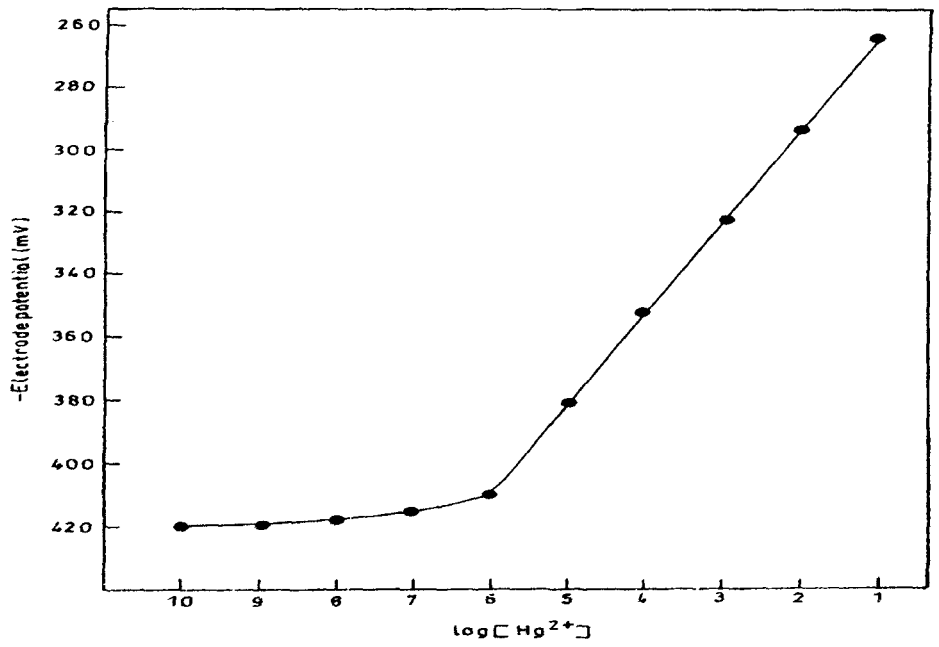

Figure 5.1 Calibration curve of poly-o-toluidine Zr(IV) phosphate membrane electrode in aqueous solutions of $Hg(NO_3)_2$

It was observed that the electrode potential (Table 5.4) remain unchanged within the pH range of 4.0-8.0 (Figure 5.2). Hence, it is ascertained that the pH range in which potential not changed is known as working pH for this electrode. The sharp change in potential at lower pH value (<3) appeared to be due to interference caused by H^+ ions (co-fluxing of H^+ ions), while at higher pH values (>9) it may be attributed to the interferences of OH^- ions (hydrolysis of Hg^{2+}).

Another important factor is the promptness of the response of the ion-selective electrode. The average response time is defined [29] as the time required for the electrode to reach a stable potential after successive immersion of the electrode in different Hg^{2+} ion solutions each having a 10-fold difference in concentration.

The response time in contact with 1×10^{-2} M Hg^{2+} ion solution was determined (Table 5.5) for the membrane electrode and the results are shown in Figure 5.3. It is shown that the response time of the membrane sensor is found to be ~5 s.

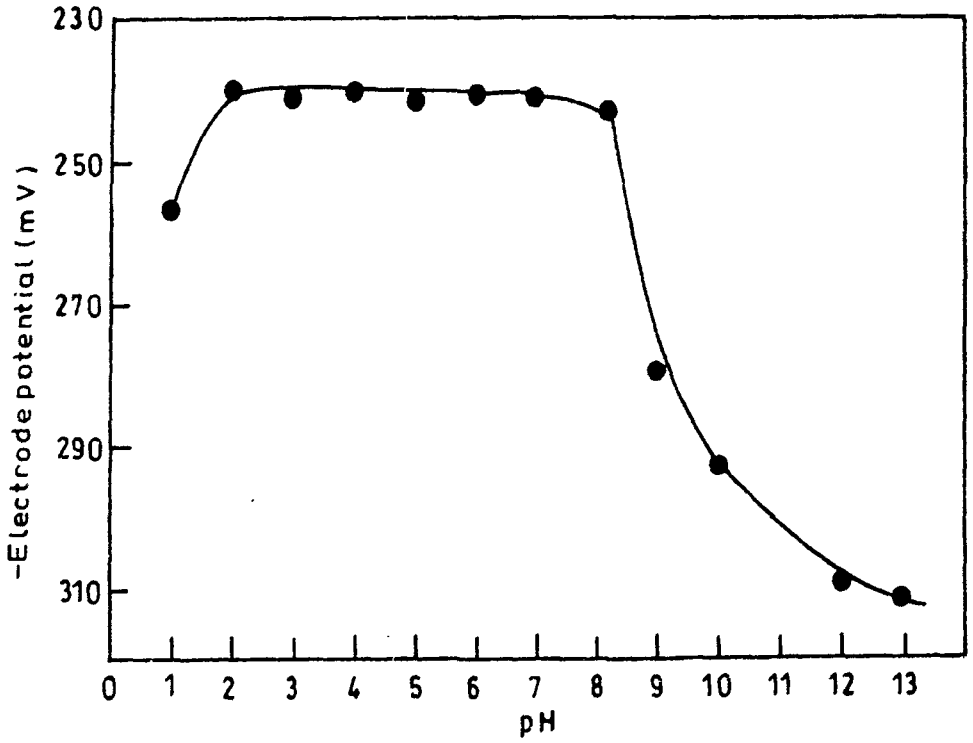

Figure 5.2 Effect of pH on the potential response of the poly-o-toluidine Zr(IV) phosphate membrane electrode $1x10^{-2}$M Hg^{2+} concentration

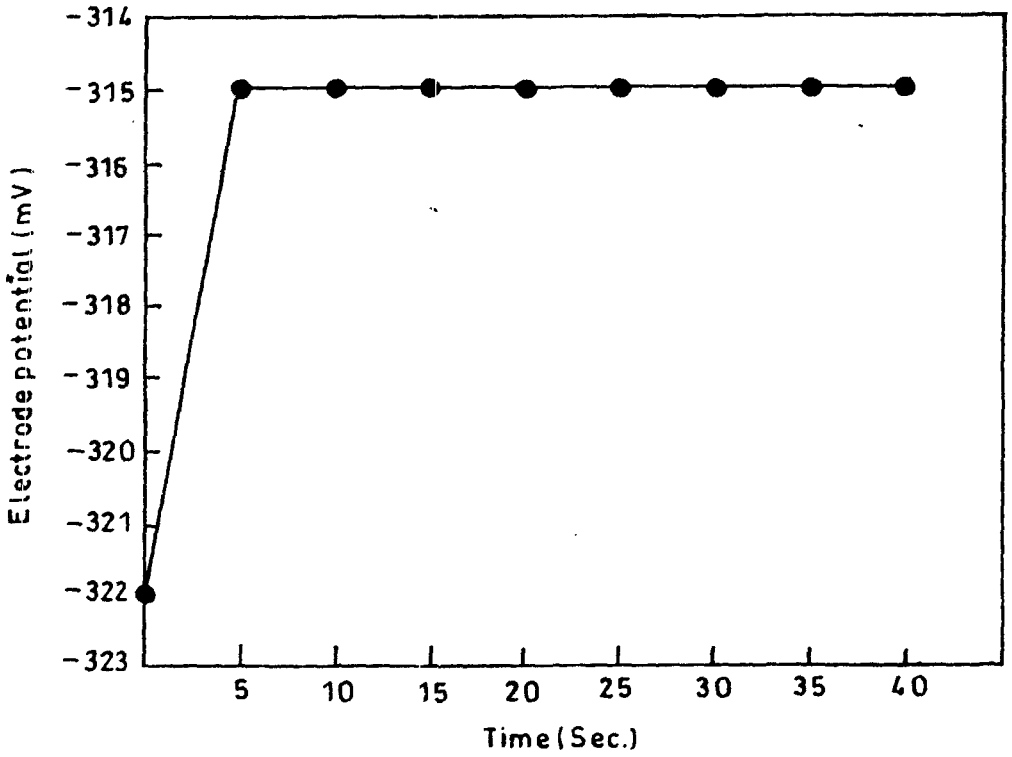

Figure 5.3 Time response curve of poly-o-toluidine Zr(IV) phosphate membrane electrode

The membrane could be successfully used upto two months without any notable drift in potential during which the potential slope is reproducible within ±1 mV per concentration decade. Whenever a drift in the potential is observed, the membrane is re-equilibrated with 0.1M $Hg(NO_3)_2$ solution for 3-4 days.

The selectivity coefficients, K_{HgM}^{pot} of various differing cations for the Hg(II) ion-selective poly-o-toluidine Zr(IV) phosphate nano-composite membrane electrode were determined, by the mixed solution method [30]. The selectivity coefficient indicates the extent to which a foreign ion (M^{n+}) interferes with the response of the electrode towards its primary ions (Hg^{2+}). By examine the selectivity coefficient data given in Table 5.6, it is clear that the electrode is selective for Hg(II) in presence of interfering cations. Since all the foreign metal ions interfere to a very little extant, these ions would not cause any significant interference in the determinations of Hg^{2+}.

The selectivity coefficients of bivalent and trivalent metal ions like Co(II), Zn(II), Cd(II), Pb(II), Ba(II), Cr(III), Fe(III) and Al(III) showed somewhat higher values and interfered to a very little extent. However Ba(II), Mg(II), Ca(II), Sr(II) and Al(III) showed very low selectivity coefficients, and hence interference was found to be

negligible. However, the values of the selectivity coefficients in case of monovalent cations, like Na(I) and K(I), is exceptionally high due to the smaller charge of the interfering ions. Therefore, despite their large selectivity coefficients, these ions would not disturb the functioning of the Hg(II)-selective membrane electrode. Thus, the results as shown in Figure 5.4 revealed that the electrode was selective for Hg(II) in the presence of interfering cations. Therefore, it is understandable the poly-o-toluidine Zr(IV) phosphate interacts relatively strongly with Hg(II) ions and can be successfully used as a sensing agent for mercury-selective electrodes.

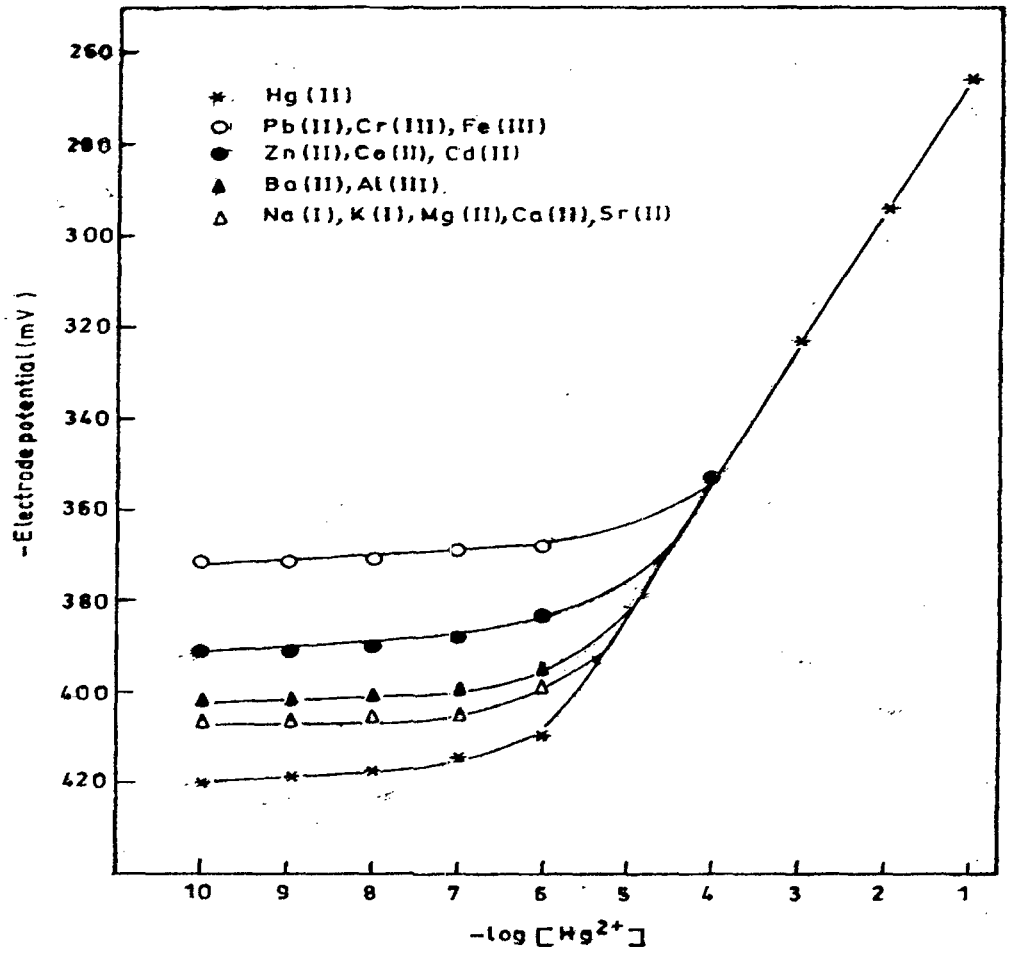

Figure 5.4 Selectivity coefficients of various interfering ions for a poly-o-toluidine Zr(IV) phosphate membrane electrode

5.5.3 Potentiometeric studies of heterogeneous poly-o-toluidine Ce(IV) phosphate nano-composite membrane electrode

Poly-o-toluidine Ce(IV) phosphate nano-composite membrane (M-2) was fabricated into ion-selective electrode and the membrane electrode was placed in 0.1M $Cd(NO_3)_2$

solution for 7 days to get it conditioned. After conditioning the electrode, the potentials for a series of standard solution of the $Cd(NO_3)_2$ in the range 10^{-10} M to 10^{-1} M were measured at a fixed concentration of Cd^{2+} ion as internal reference solution. The choice of Cd^{2+} ions depends on its distribution behavior patterns.

After conditioning of the electrode, the potentials for a series of standard solution of the $Cd(NO_3)_2$ in the range 10^{-10} M to 10^{-1} M were measured, maintaining a fixed concentration of Cd^{2+} ion as internal reference solution. It was observed that the most favorable concentration of reference solution, for smooth functioning of the proposed membrane sensor is 0.1M.

Potential measurements of the heterogeneous precipitate based membrane electrodes was plotted against the selected concentration of the Cd^{2+} ions (Figure 5.5) and gives linear response in the range 1×10^{-1} M to 1×10^{-6} M. Suitable concentration were chosen for sloping portion of the linear curve. The limit of detection was determined from the intersection of the two extrapolated segments of the calibration graph [27] was found to be 1×10^{-6} M, and thus the working concentration range is found to be 1×10^{-1} M to 1×10^{-6} M for Cd^{2+} ions with a *Nerstian* slope of 24.01 mV per decade change in Cd^{2+}ion concentration, the slope value is close to *Nerstian* value, 29.6±3 mV per concentration decade for divalent cation. Below 1×10^{-6} M, none linear response was observed that could be used for analytical applications [28].

In order to investigate pH effect on the potential response of the electrode, the potential were measured for a fixed concentration of Cd^{2+} ions in different pH values. The measurements were carried out at different concentrations (1×10^{-2} M and 1×10^{-3} M) of Cd^{2+} ion solutions but the results were recorded only for 1×10^{-2} M ion solutions (Table 5.4).

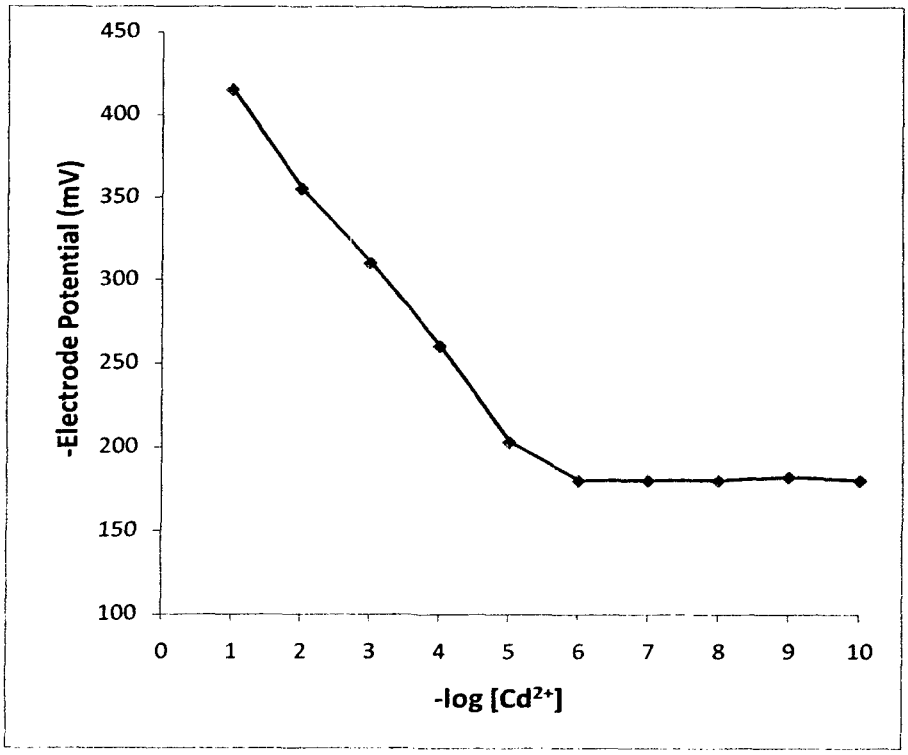

Figure 5.5 Calibration curve of poly-o-toluidine Ce(IV) phosphate membrane electrode in aqueous solution of $Cd(NO_3)_2$

It was observed that the electrode potential remain unchanged within the pH range of 4.0-7.0 (Figure 5.6). Hence, it is ascertained that the pH range in which potential not changed is known as working pH for this electrode. The sharp change in potential at lower pH value (<3) appeared to be due to interference caused by H^+ ions (co-fluxing of H^+ ions) while at higher pH values(> 9) it may be attributed to the interference of OH^- ions (hydrolysis of Cd^{2+})

Another important factor is the promptness of the response of the ion-selective electrode. The average response time is defined [29] as the time required for the electrode to reach a stable potential after successive immersion of the electrode in different Cd^{2+} ion solutions each having a 10-fold difference in concentration.

The response time in contact with 1×10^{-2} M Cd^{2+} ion solution was determined (Table 5.5) for the membrane electrode and the results are shown in (Figure 5.7). It is shown that the response time of the membrane sensor is found to be ~20 s.

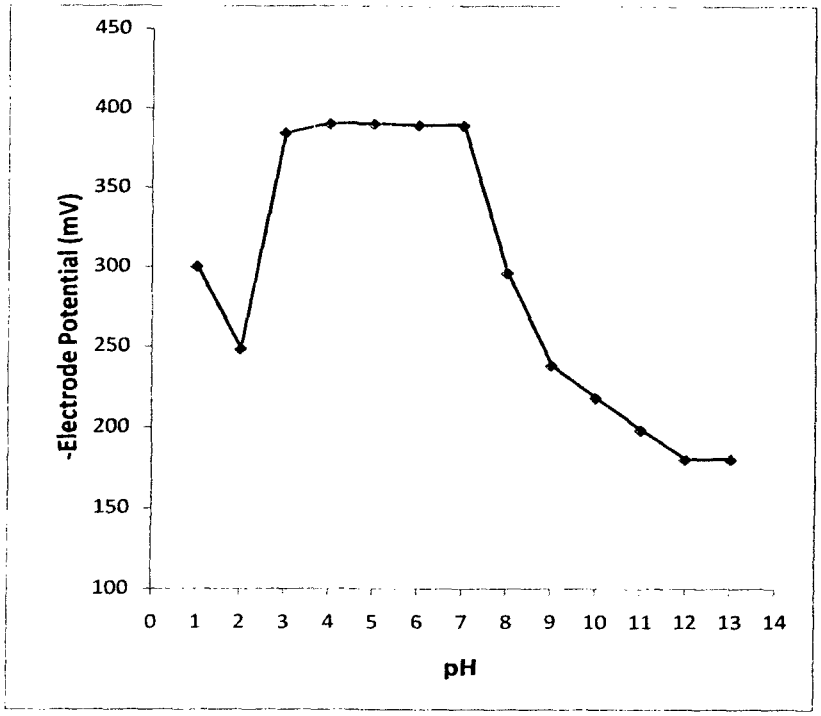

Figure 5.6 Effect of pH on the potential response of the poly-o-toluidine Ce(IV) phosphate membrane electrode at 10^{-2} M concentration

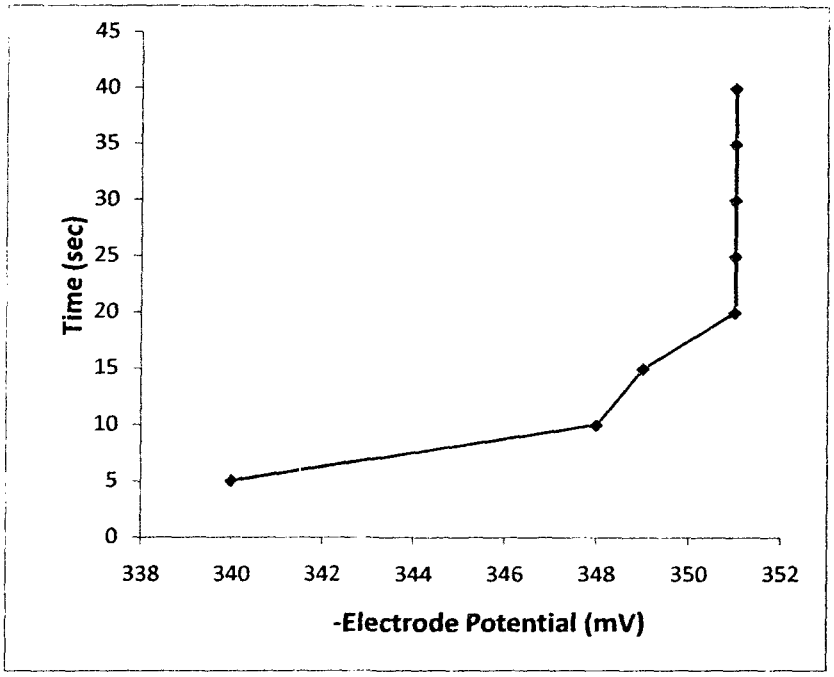

Figure 5.7 Time response curve of poly-o-toluidine Ce(IV) phosphate

The membrane could be successfully used upto three months without any notable drift in potential during which the potential slope is reproducible within ±1 mV per concentration decade. Whenever a drift in the potential is observed, the membrane is re-equilibrated with 0.1M $Cd(NO_3)_2$ solutions for 3-4 days.

The selectivity coefficients, $K_{Cd,M}^{pot}$ of various differing cations for the Cd(II) ion selective poly-o-toluidine Ce(IV) phosphate nano-composite membrane electrode were determined, by the mixed solution method [30]. The selectivity coefficient indicates the extent to which a foreign ion (M^{n+}) interferes with the response of the electrode towards its primary ions (Cd^{2+}). By examine the selectivity coefficient data given in Table 5.6, it is clear that the electrode is selective for Cd(II) in presence of interfering cations. Since all the foreign metal ions interfere to a very little extant, these ions would not cause any significant interference in the determinations of Cd^{2+}.

5.5.4 Potentiometric studies of fibrous Nylon-6,6 Sn(IV) phosphate composite membrane electrode

Nylon-6,6 Sn(IV) phosphate composite membrane (M-3) was fabricated into ion-selective electrode and the membrane electrode was placed in 0.1M $Hg(NO_3)_2$ solution for 7 days to get it conditioned. After conditioning the electrode, the potentials for a series of standard solution of the $Hg(NO_3)_2$ in the range 10^{-10} M to 10^{-1} M were measured at a fixed concentration of Hg^{2+} ion as internal reference solution. The choice of Hg^{2+} ions depends on its distribution behavior patterns.

After conditioning of the electrode, the potentials for a series of standard solution of the $Hg(NO_3)_2$ in the range 10^{-10} M to 10^{-1} M were measured, maintaining a fixed concentration of Hg^{2+} ion as internal reference solution. It was observed that the most favorable concentration of reference solution, for smooth functioning of the proposed membrane sensor is 0.1M.

The potentiometric response of the membrane electrode prepared from membrane sample M-3 over a wide concentration range 10^{-1} - 10^{-9} is shown in Figure 5.8. The electrode showed a linear Nernstian response for Hg(II) ions in the concentration range $1 \times 10^{-1} - 1 \times 10^{-7}$ M with an over Nernstian slope of 28.09 mV per decade change in concentration. The limit of detection of the electrode, as determined according to the IUPAC recommendation [31,32] form the intersection of two segments of calibration curve, was 1×10^{-7} M. An over-Nernstian response in electrode of this kind is common [33-35].

For the present Nylon-6,6 Sn(IV) phosphate membrane electrode, it was observed that the measured potential of Hg^{2+} ions in a given concentration range of $10^{-1} - 10^{-9}$ M was reproducible within ±1 mV, and there was no significant change in the slope of the

Nernst plot during the experiment over a time period of 1 months. This suggests a longer electrode life and a stable electrode performance.

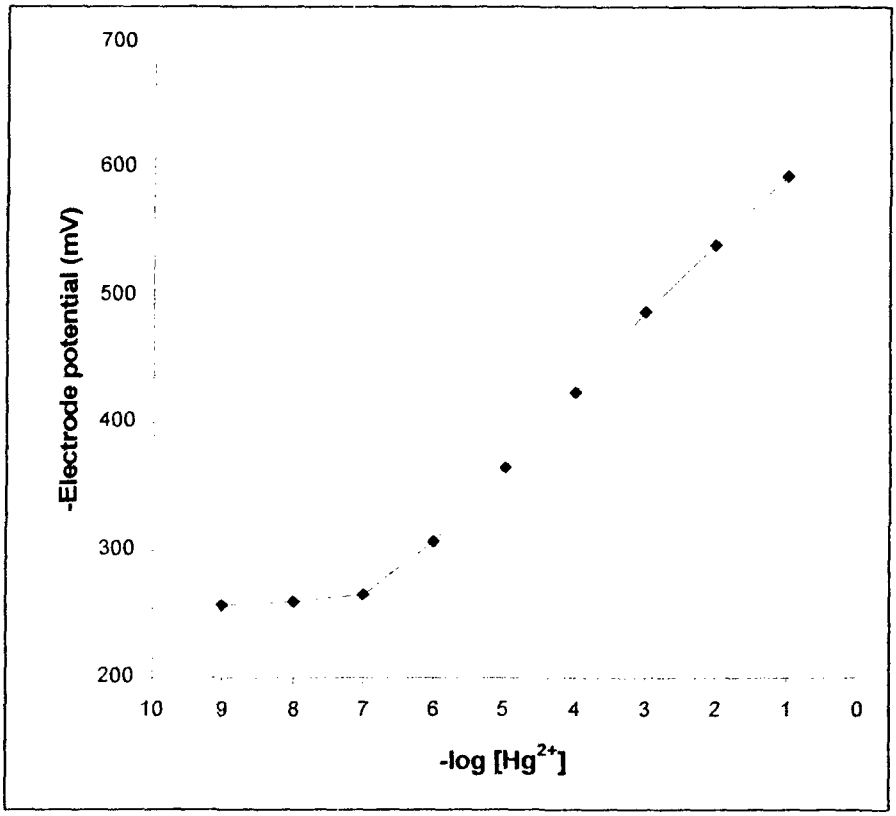

Figure 5.8 Calibration curve of Nylon-6,6 Sn(IV) phosphate membrane electrode in aqueous solutions of $Hg(NO_3)_2$

It is clear that the pH influenced the response characteristics of the proposed Hg(II) ion-selective membrane electrode that the potential (Table 5.4) remained unchanged within the pH range 4 – 7 (Figure 5.9). After that pH, the electrode behaved in an erratic manner, which may be because mercury ions formed a hydroxyl complex and precipitated. Thus, we can say that the optimum pH range of operation of this electrode was pH 4 - 7.

Another important factor is the promptness of the response of the ion-selective electrode. The average response time is defined [29] as the time required for the electrode to reach a stable potential after successive immersion of the electrode in different Hg^{2+} ion solutions each having a 10-fold difference in concentration.

The response time in contact with 1×10^{-2} M Hg^{2+} ion solution was determined (Table 5.5) for the membrane electrode and the results are shown in Figure 5.10. It is shown that the response time of the membrane sensor is found to be ~40 s.

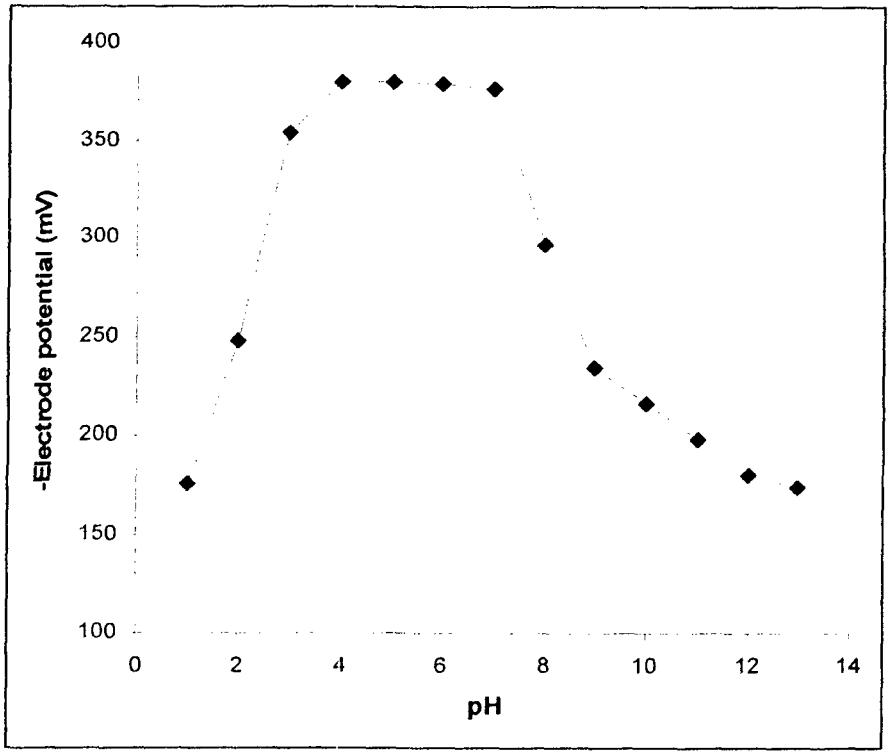

Figure 5.9 Effect of pH on the potential response of the Nylon-6,6 Sn(IV) phosphate membrane electrode $1x10^{-2}M\ Hg^{2+}$ concentration

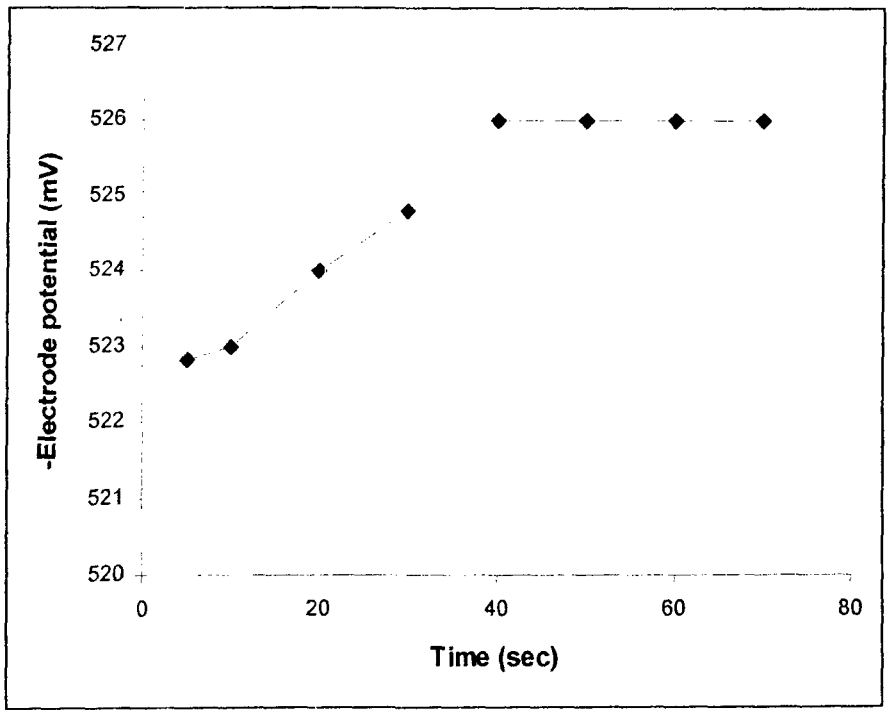

Figure 5.10 Time response curve of Nylon-6,6 Sn(IV) phosphate membrane electrode

The membrane could be successfully used upto three weeks without any notable drift in potential during which the potential slope is reproducible within ±1 mV per concentration decade. Whenever a drift in the potential is observed, the membrane is re-equilibrated with 0.1 M $Hg(NO_3)_2$ solution for 3-4 days.

The selectivity coefficients, K_{HgM}^{pot} of various differing cations for the Hg(II) ion selective Nylon-6,6 Sn(IV) phosphate composite membrane electrode were determined, by the mixed solution method [30]. The selectivity coefficient indicates the extent to which a foreign ion (M^{n+}) interferes with the response of the electrode towards its primary ions (Hg^{2+}). By examine the selectivity coefficient data given in Table 5.6, it is clear that the electrode is selective for Hg(II) in presence of interfering cations. Since all the foreign metal ions interfere to a very little extant, these ions would not cause any significant interference in the determinations of Hg^{2+}.

The selectivity coefficients of bivalent and trivalent metal ions, like Co(II), Zn(II), Cd(II), Pb(II), Cu(II) and Fe(III) showed somewhat higher values and interfered to a very little extent. However Ba(II), Mg(II), Sr(II), Ni(II) and Al(III) showed very low selectivity coefficients, and hence interference was found to be negligible. Therefore, despite their large selectivity coefficients, these ions would not disturb the functioning of the Hg(II)-selective membrane electrode. Thus, the results as shown in Figure 5.11 revealed that the electrode was selective for Hg(II) in the presence of interfering cations. Therefore, it is understandable the Nylon-6,6 Sn(IV) phosphate interacts relatively strongly with Hg(II) ions and can be successfully used as a sensing agent for mercury-selective electrodes

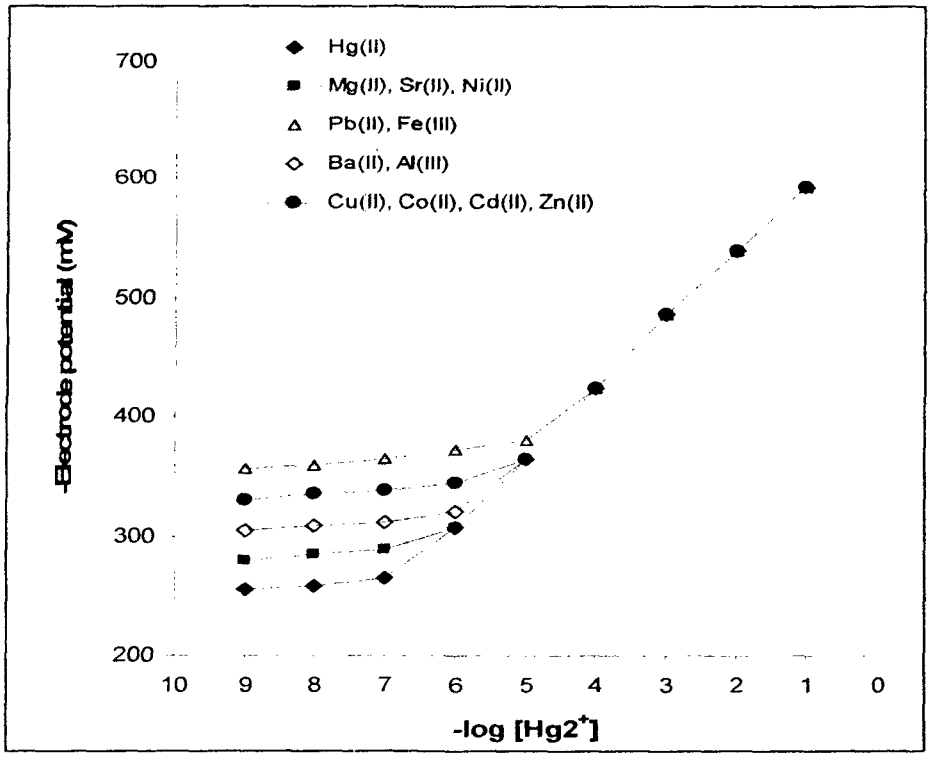

Figure 5.11 Selectivity coefficients of various interfering ions for Nylon-6,6 Sn(IV) phosphate membrane electrode

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Chapter-6

Analytical and Electroanalytical Applications of Poly-o-toluidine Zr(IV) phosphate, Poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate Cation-Exchangers

6.1 Introduction

Heavy metals when present in water in concentrations exceeding the permitted limits are injurious to the health. Water pollution has been seriously affecting the life of humans, plants as well as animals. The eco-system of rivers, streams, lakes, seas and oceans is also getting deteriorated due to the contamination of water through various sources. Hence, it is very important to treat such waters to remove the metal ions present before it is supplied for any useful purpose. When we need to remove a particular ion in presence of other, we need a material specific for that particular metal ion and a devise to determine the concentration level. Thus by synthesizing new 'organic-inorganic' composite ion-exchangers having selectivity for particular metal ion, we can separate the undesired metal from the effluents such as Cd, Pb, Hg, Cr, Ni, Sn, Cu, Co, As and Zn. A large number of such composite materials possessing the selectivity for heavy toxic metal ions have been prepared in our laboratory and are being utilized in environmental water pollution analysis [1-8]. Secondly 'organic-inorganic' electrically conducting composite ion-exchangers can be used in the preparation of sensitive and selective ion-sensors, potentiometer sensors, chemical sensors, or more commonly ion-selective electrodes (ISEs) for the determination of heavy toxic metal ions in the waste water samples. Therefore, these composite ion-exchangers have well established their position in separation science and technology, and have been employed in the selective separation and preconcentration of metal ions as well as recovery of heavy toxic metals from various waste effluents to decrease the pollution load in the environment [9-17].

Use of mercury has also been declined due to the acute toxicity of the inorganic and organic forms of this metal. Its applications include as a cathode in chloroalkali cells, as a fungicide, as a catalyst for polymer production and in the cosmetics and pharmaceutical industry are still important. The inorganic form of mercury is readily converted via biotic and abiotic processes in aquatic habitats to form alkylated lipophilic neurotoxic species which bioaccumulate in freshwater and marine organisms. Inorganic mercury is typically found at concentrations <0.5 pg/L in ground and surface waters. The predominant organic forms are methyl-, ethyl- and phenylmercury, which can biomagnify through the food chain for more readily than inorganic forms and result in chronic human exposure. The ingestion of fish and related products are a primary source of exposure, and there has been alarming evidence of the presence of methyl-mercury in fish-based foods.

Cadmium is a toxic heavy metal that appears in the environment mainly due to industrial processes. Besides natural exposure from soils or earth crust with high content

of cadmium, anthropogenic processes like combustion of coal and mineral oil, smelting, mining, alloy processing, paint industries, etc. are the major sources of lead and cadmium to the people in the vicinity of the industrial areas. Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies for examples liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. Another important source of cadmium emission is the production of artificial phosphate fertilizers. Cadmium strongly adsorbs to organic matter in soils. United States Environmental Protection Agency (EPA) has found cadmium to potentially cause the following health effects when people are exposed to it at levels above the minimum concentration level (MCL) for relatively short periods of time: nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock and renal failure and in long-term cadmium has the potential to cause the following effects from a lifetime exposure at levels above the MCL: kidney, liver, bone and blood damage [18].

The WHO guidelines for drinking water quality stipulate allowable concentrations of 0.01 and 0.001 mg L^{-1} for Hg(II) and Cd(II).

Since these composite materials i.e. poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate were found highly selective for mercury and cadmium respectively as shown from the selectivity studies performed in Chapter-3 (Section 3.3.6); the utility of these cation-exchangers have been explored for the quantitative separations of Hg^{2+} and Cd^{2+} from some binary mixtures as well as removal of these toxic metals from some synthetic samples. Therefore, in this chapter we have studied some analytical and environmental applications of these composite materials in separation of metal ions, as adsorbent and as an ion-selective membrane electrode.

6.2 Experimental

6.2.1 Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-merck, Ciba-Geigy and Qualigens (India Ltd.). All other reagents and chemicals were of analytical reagent grade. A digital pH-meter (Elico LI-10, India), a temperature controlled shaker and a digital potentiometer (Equiptronics EQ 609, India) with saturated calomel electrodes as reference electrodes were used.

6.2.2 Preparation of poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate composite cation-exchangers: their membranes and ion-selective electrodes

Various samples of 'organic-inorganic' composite cation-exchange materials 'poly-o-toluidine Zr(IV) phosphate', 'poly-o-toluidine Ce(IV) phosphate' and 'Nylon-6,6 Sn(IV) phosphate'were prepared as described in Chapter - 2 (Section 2.2.3.). But the sample S-5 (Table 2.1), sample T-4 (Table 2.2) and sample P-4 (Table 2.3) were selected for the studies of their analytical applications as potentiometric sensors. The preparation of ion-exchange membranes and fabrication of ion-selective electrodes were done as described in Chapter- 5 (Section 5.2.4 and 5.3.5).

6.2.3 Analytical applications of the composites

6.2.3.1 Quantitative separations of metal ions using composite cation-exchangers

On the basis of K_d values (distribution studies) of sample S-5, sample T-4 and sample P-4 (described in Chapter 3 (Section 3.3.6), these samples were selected to achieve quantitative binary separations of some important metal ions of analytical utility on poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate columns. 1g of the materials S-5, T-4 and P-4 (~125 μm particle size) in H^+ form were used for column separations in two different glass tubes having an internal diameter of ~0.6 μm and a height of 35 cm. The columns were washed thoroughly with DMW. The mixture of two metal ions having initial concentrations of 0.01M each of definite volume was loaded on the both columns and allowed for one hour to absorb the metal ions on the exchangers. The mixture was then passed on to the columns gently (maintaining a flow rate of 2-3 drops per minute) till the level was above the surface of the 'materials'. After recycling two or three times to ensure complete adsorption of the mixture on column heads, the separations were achieved by passing a suitable solvent with a flow rate of 1 ml/min through the columns as eluent. The metal ions in the effluent were determined quantitatively by AAS and EDTA titration.

6.2.3.2 Preparation of Nylon-6,6 Sn(IV) phosphate-PAN indicator strips

About 0.5 g fibrous composite material (Nylon-6,6 Sn(IV) phosphate) was dipped in PAN indicator for 24 hr. The excess indicator was washed with DMW and the material was dried at 40 °C in an oven. The material was placed under hydraulic pressure machine at

25 KN pressure to obtain fibrous strip. A drop of different concentration of some heavy metals such as Cu(II), Pb(II), Hg(II), Fe(II) was placed on strip. The color change was observed from the yellowish strip as shown in Table 6.1.

Table 6.1 Change in colour of fibrous PAN strip with different concentration of metal ions

Concentration	Cu(II)	Pb(II)	Hg(II)	Fe(II)
200 ppm	Dark red	Dark red	Red	Red
100 ppm	Red	Red	Red	Red
50 ppm	Light red	Red orange	orange	Yellow
10 ppm	Red orange	orange	orange	Yellow
5 ppm	Red orange	Yellow	Yellow	Yellow
2 ppm	Yellow	Yellow	Yellow	Yellow

6.2.3.3 Determination of Hg^{2+} and Cd^{2+} by potentiometric titrations using the poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate membrane electrodes

The mercury and cadmium selective membrane electrodes were employed as indicator electrodes in the titration of 1.0×10^{-2} M $Hg(NO_3)_2$ and 1.0×10^{-2} M $Cd(NO_3)_2$ solutions, respectively against 0.005M EDTA solution as a titrant. For this, 5 ml of $Hg(NO_3)_2$ and $Cd(NO_3)_2$ solutions were pipette out in two different beakers. The volume of each beaker was raised upto 20 ml by DMW. These solutions were titrated with EDTA solution and electrode potential was measured after each addition of 0.5 ml EDTA solution. The necessary adjustment of pH (~4) was made before adding the titrant. Potential values were plotted against the volume of EDTA used.

6.3 Results and Discussion

6.3.1 Quantitative separation of metal ions using composite cation-exchangers

On the basis of distribution studies, the most promising property of these materials was found to be high selectivity towards Hg(II) and Cd(II) (major polluting elements in the environment) indicating importance in environmental studies.

The separation capability of the material poly-o-toluidine Zr(IV) phosphate has been demonstrated by achieving some important binary separations of different synthetic metal mixtures involving Hg(II), for example: Hg(II)-Cu(II), Hg(II)-Co(II), Hg(II)-Pb(II), Hg(II)-Cd(II) and Hg(II)-Fe(III). The sequential elution of ions from the column depends upon the stability of metal-eluting ligand (eluent). It was observed that Hg(II) retained strongly on the cation-exchanger column. The order of elution and eluents used for some representative binary separations are also illustrated in Figure 6.1. The separations are quite sharp and recovery is quantitative and reproducible. It was also observed from the distribution studies that the cation-exchanger was also found to be selective for Hg(II).

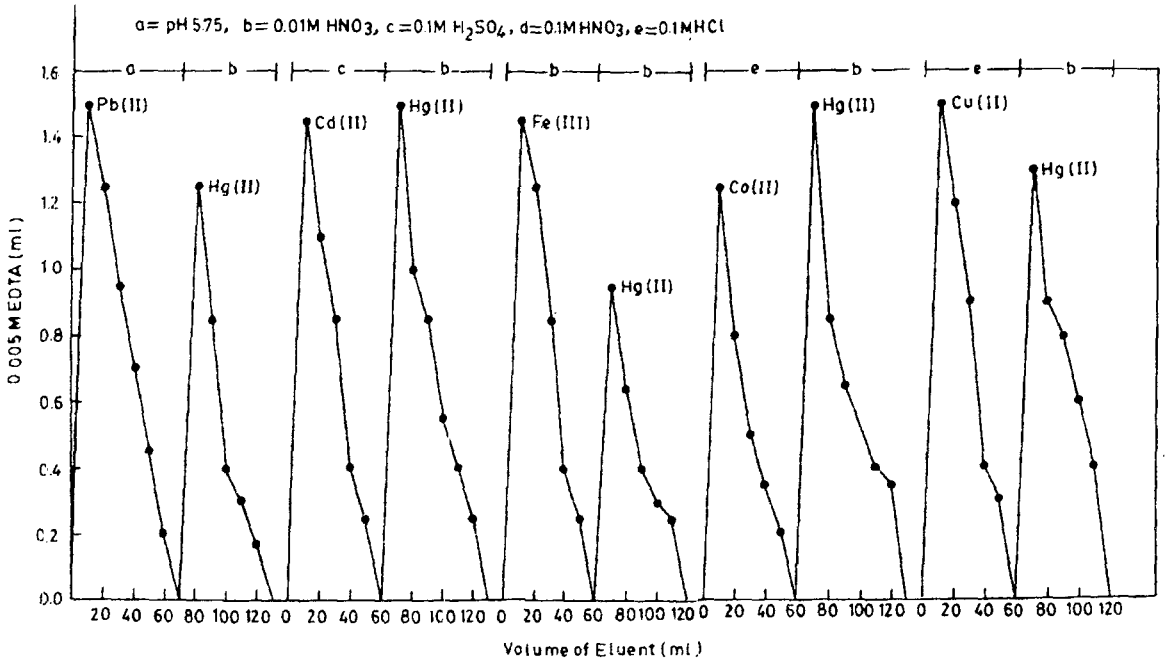

Figure 6.1 Binary separations of Hg(II) from Pb(II), Cd(II), Fe(III), Co(II) and Cu(II) on poly-o-toluidine Zr(IV) phosphate column

On the basis of distribution studies, the most promising property of the composite cation-exchanger Nylon-6,6 Sn(IV) phosphate was found to be the high selectivity towards Hg(II). The separation capability of the material has been demonstrated by

achieving some important binary separations of different synthetic metal mixtures involving Hg(II), for example: Hg^{2+}-Mg^{2+}, Hg^{2+}-Zn^{2+}, Hg^{2+}-Fe^{3+}, Hg^{2+}-Al^{3+} and Hg^{2+}-Pb^{2+}. The sequential elution of ions from the column depends upon the stability of metal-eluting ligand (eluent). The order of elution and eluents used for these separations are also illustrated in Figure 6.2. The separations are quite sharp and recovery is quantitative and reproducible. It may also be observed from the distribution studies that the cation-exchanger was also found to be selective for Hg(II).

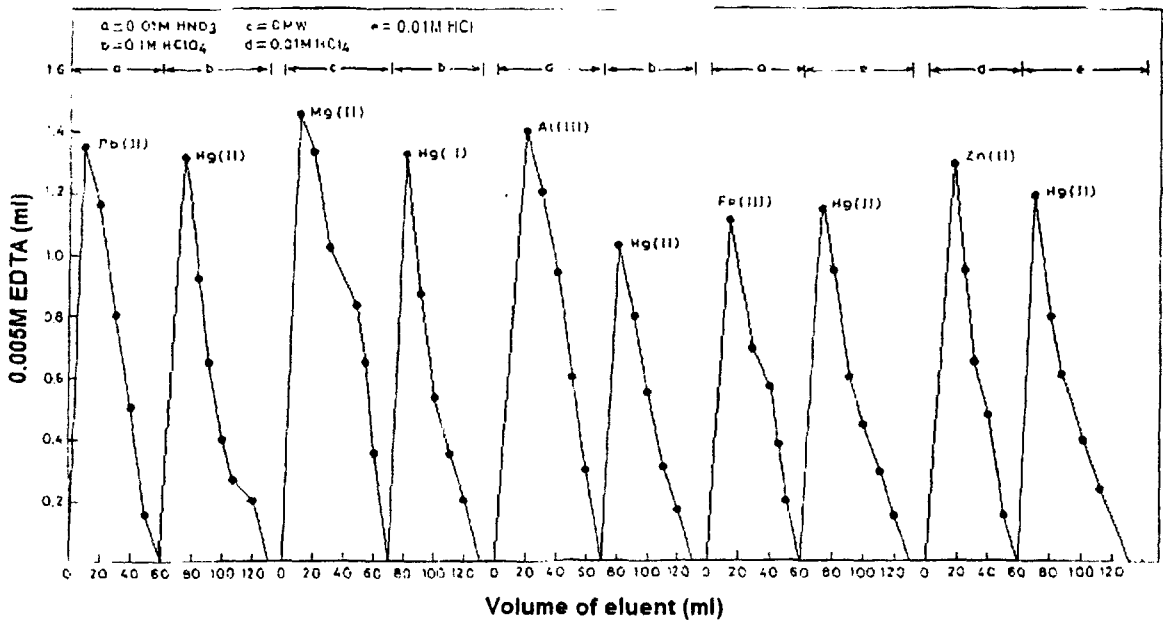

Figure 6.2 Binary separations of Hg(II) from Mg(II), Fe(III), Zn(IV), Al(III) and Pb(II) on Nylon-6,6 Sn(IV) phosphate composite columns

6.3.2 Determination of Hg^{2+} and Cd^{2+} by potentiometric titrations using poly-o-toluidine Zr(IV) phosphate, poly-o-toluidine Ce(IV) phosphate and Nylon-6,6 Sn(IV) phosphate membrane electrodes

The analytical utility of poly-o-toluidine Zr(IV) phosphate membrane electrode has been established by employing it as an indicator electrode in the potentiometeric titration of a 0.01M $Hg(NO_3)_2$ solution against EDTA solution as titrants. The results are shown in Figure 6.3. For this purpose, 5 ml portions of $Hg(NO_3)_2$ solutions were pippeted out in three different beakers, and the volume of each beaker was raised up to 20 ml by adding demineralized water. The solutions were titrated against EDTA solution, the electrode potential was measured after each addition of 0.5 ml. The necessary adjustment of pH (~ 4) was made before adding the titrant. The addition of titrants caused a decrease in the

potential as a result of a decrease in the free Hg(II) ion concentration due to the formation of a complex with titrants. The amount of Hg(II) ions in solutions can be accurately determined from the resulting neat titration curves, providing a sharp end point. Potentiometric titrations of Hg(II) were also successfully carried out in the presence of 1 × 10^{-5} M Ni(II), Cu(II) and Zn(II), hence demonstrating its applications as a sensor developed for the potentiometric determination of Hg(II) in mixtures. Poly-o-toluidine Zr(IV) phosphate, Hg^{2+} ion-selective membrane electrodes were also applied to direct measurements of Hg^{2+} in the drain water collected from Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India. The samples were collected by a routine technique from five different locations of drains, and preserved with HNO_3, stored in glass bottles and analyzed within 12 h after collection. Since the samples contained particulate matters, they were centrifuged, and the potentials were measured after adjusting the pH to ~ 4 with HNO_3 or NH_3. Three replicate measurements were made to obtain the Hg(II) contents in five samples with this electrode using the membrane sensor's calibration graph. The concentration of mercury in the sample was 10^{-3} M and the reproducibility of the results was checked up to three times.

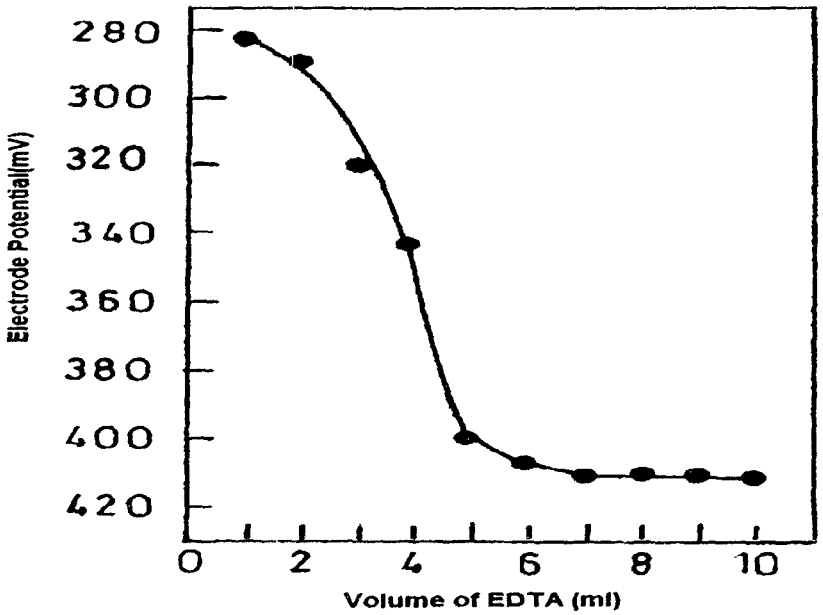

Figure 6.3 Potentiometric titration of Hg(II) against EDTA solution using poly-o-toluidine Zr(IV) phosphate membrane electrode

The practical utility of the proposed Poly-o-toluidine Ce(IV) phosphate membrane sensor assembly was tested by its use as an indicator electrode in the potentiometeric titration of 0.01M $Cd(NO_3)_2$ solution with EDTA. The addition of EDTA causes a

decrease in potential as a result of the decrease in the free Cd(II) ions concentration due to its complexation with EDTA (Figure 6.4). The amount of Cd(II) ions in solution can be accurately determined from the resulting neat titration curve providing a sharp rise in the titration curve at the equivalence points.

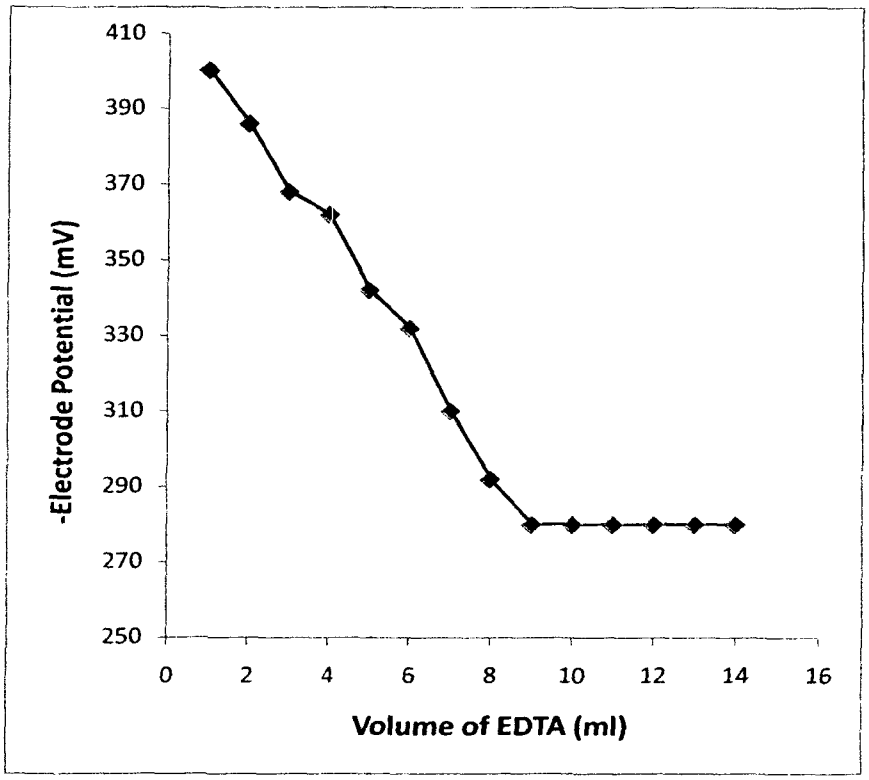

Figure 6.4 Potentiometric titration of Cd(II) against EDTA solution using poly-o-toluidine Ce(IV) phosphate membrane electrode

The practical utility of the proposed Nylon-6,6 Sn(IV) phosphate membrane sensor assembly was tested by its use as an indicator electrode in the potentiometeric titration of 0.01M $Hg(NO_3)_2$ solution with EDTA. The addition of EDTA causes a decrease in potential as a result of the decrease in the free Hg(II) ions concentration due to its complexation with EDTA (Figure 6.5). The amount of Hg(II) ions in solution can be accurately determined from the resulting neat titration curve providing a sharp rise in the titration curve at the equivalence points.

Nylon-6,6 Sn(IV) phosphate is a white color fibrous type material. This material can be also used in making indicator strips for qualitative and approximately quantitative determination of heavy metals. PAN indicator strips of Nylon-6,6 Sn(IV) phosphate suggest the sensitivity of some heavy metals like Cu(II), Pb(II), Hg(II), Fe(II) in the concentration range of 2 ppm to 200 ppm (Table 6.1). The change in color may suggest

an approximate amount of heavy metals in an unknown sample. Photograph of a single fiber of Nylon-6,6 Sn(IV) phosphate and a PAN indicator strips of the composite cation-exchanger are shown in Figure 6.6.

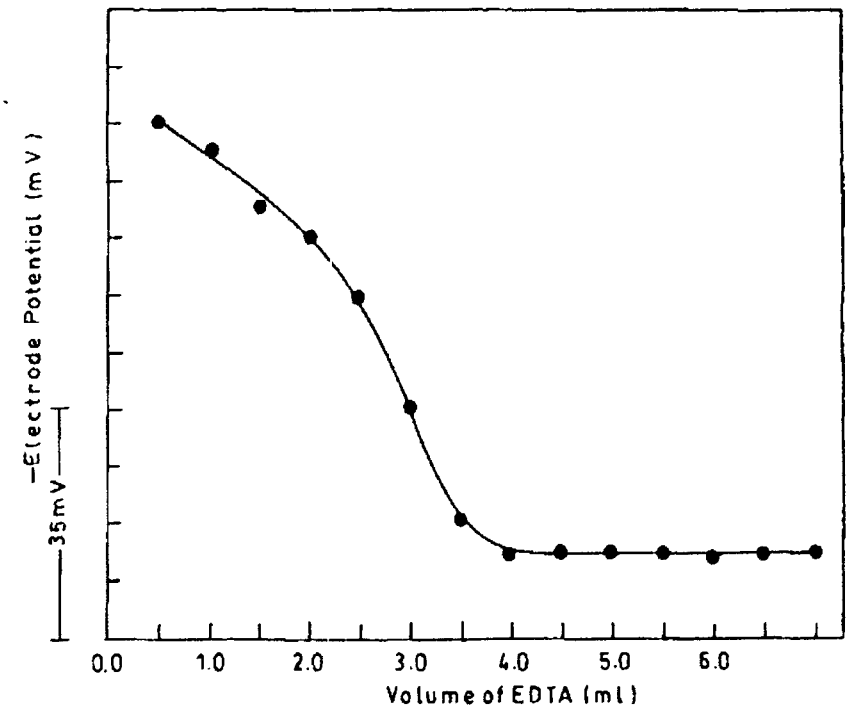

Figure 6.5 Potentiometric titration of Hg(II) against EDTA solution using Nylon-6,6 Sn(IV) phosphate membrane electrode

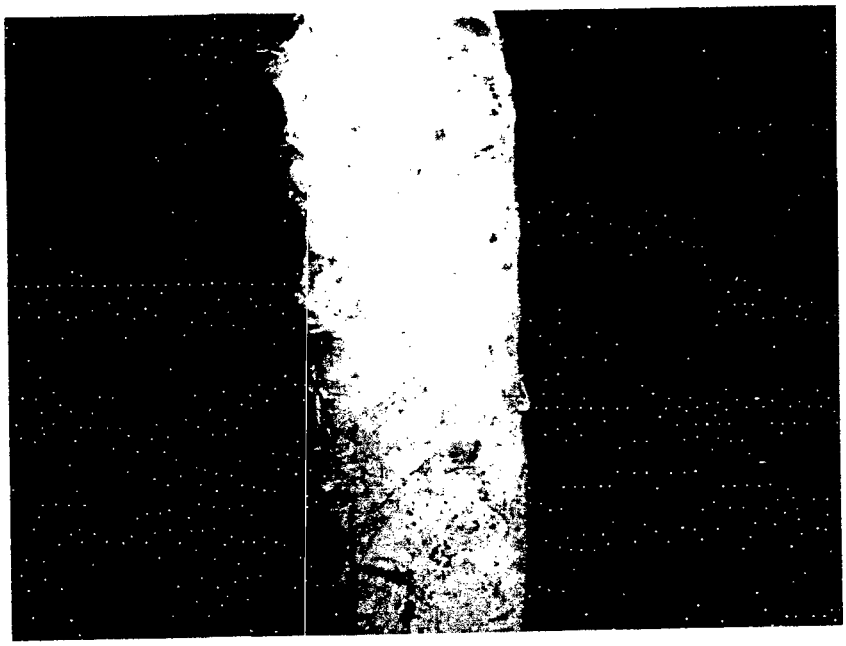

Figure 6.6 Photograph of the Strip of Nylon-6,6 Sn(IV) phosphate composite cation-exchanger

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Chapter-7

Adsorption and Electroanalytical studies on Nano-Composite Poly-o-toluidine Zr(IV) phosphate for Ziram (Zinc(II) dimethyldithiocarbamate)

7.1 Introduction

Pesticides of the carbamate family have been progressively replacing more persistent species (mainly organophosphates) due to their low persistence in the environment, biological activity and large spectrum of utilization. They are used as insecticides, fungicides, nematocides, miticides and molluscocides. Dithiocarbamates are widely used in agriculture as fungicide and in rubber industry as vulcanization accelerators and antioxidants. Metal salts of dithiocarbamates are more effective as fungicides because the toxicity of the dithiocarbamate is increased due to the presence of metal in it. Dithiocarbamates have also been determined in vegetable foodstuffs using high-performance liquid chromatography [1], extraction voltammetry [2] and titrimetry [3]. Capillary electrophoresis was used by Rossi and Rotilio [4] for the qualitative and quantitative analysis of different carbamates, thiocarbamates and dithiocarbamates. However, all these methods suffer from the following disadvantages (i) methods other than gas chromatography are indirect, time-consuming and sensitivity is low, and (ii) gas chromatographic methods are sensitive, but suffers from a lack of selectivity since all dithiocarbamate pesticides evolve carbon disulfide on acid hydrolysis.

Inorganic ion-exchangers have been used for the exchange of metal ions [5] and these materials have also shown good adsorption behavior of some pesticides [6-9]. Organic-inorganic composite ion-exchange materials were found chemically and mechanically more stable than inorganic ion-exchange materials. These materials have shown good ion-exchange capacity [10] and successfully been used in making ion selective electrode [11-13]. It is interesting to use organic-inorganic composite materials in adsorption studies of pesticides. Such adsorption studies of pesticides on composite materials can help us in making pesticide sensitive membrane electrode that can be used to determine pesticide in trace amounts in the given sample of polluted water. In the present study poly-o-toluidine Zr(IV) phosphate, a nano-composite cation-exchanger is used for the adsorption studies of Ziram and some important thermodynamic parameters were also determined.

Ziram is an agricultural fungicide. It may be applied to the foliage of plants, but it is also used as a soil and/or seed treatment. Ziram is used primarily on almonds and stone fruits. It is also used as an accelerator in manufacturing rubber, packaging materials, adhesives and textiles. Another use of the compound is as a bird and rodent repellent. Ziram can cause skin and mucous membrane irritation. Humans with prolonged

inhalation exposure to ziram have developed nerve and visual disturbances [14]. Ziram is corrosive to eyes and may cause irreversible eye damage [15].

Ziram is also determined by converting it into molybdenum [16] and copper [17,18] complexes. The extraction of the molybdenum complex is slow, and complexation occurs in acid medium. A simple, rapid, and sensitive spectrophotometric method based on the conversion of Ziram into the copper-dimethyldithiocarbamate complex to determining Ziram is applied in the present work. However the main objective of the present research work is to developed electroanalytical method by making Ziram [zinc(II) bis(dimethyldithiocarbamate)] sensitive membrane electrode to determine Ziram in traces amounts in water.

7.2 Experimental

7.2.1 Equipment and reagents

A digital pH meter (Elico, India), potentiometer and a Elico SL 164 Double Beam UV-visible spectrophotometer were used. 0.1M solutions of Zirconium oxychloride ($ZrOCl_2.8H_2O$) and phosphoric acid (H_3PO_4) of different molarities were prepared in 4M HCl and demineralised water (DMW) respectively. Solutions of 20% (v/v) o-toluidine (C_7H_9N) and 0.4M Ammonium persulphate ($(NH_4)_2S_2O_8$) were prepared in 2M HCl.

7.2.1.1 Preparation of Ziram solutions

A stock solution of Ziram (1 g/L) was prepared by dissolving 100 mg of this in NaOH (0.1N) and diluting to 100 mL in a volumetric flask and further dilutions done with 0.1 N NaOH as desired. Copper sulphate (1.0 g/L) was prepared by dissolving 0.1 g in 100 mL of distilled water, which was then acidified, with 0.1 mL of conc. sulphuric acid. Acetate buffer was prepared in distilled water by dissolving sodium acetate trihydrate (68 g; AR grade, Merck) in water (400 mL) and adjusting the pH to 4.5 by adding glacial acetic acid (25–30 mL, AR grade, Merck,) and making up the total volume to 500 mL.

7.2.2 Preparation of poly-o-toluidine Zr(IV) phosphate composite cation-exchange material (adsorbent)

The nano-composite cation-exchanger was prepared by the sol-gel mixing of poly-o-toluidine, an organic polymer, into the inorganic precipitate of zirconium(IV) phosphate. In this process, when the gels of poly-o-toluidine were added to the white inorganic

precipitate of zirconium(IV) phosphate with a constant stirring, the resultant mixture were turned slowly into a greenish black colored slurries. The resultant greenish black colored slurries were kept for 24 hours at room temperature.

Now the poly-o-toluidine based composite gels were filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of ammonium persulphate. The washed gel dried over P_2O_5 at 40 °C in an oven. The dried product was washed again with acetone to remove oligomers present in the material, and dried at 40 °C in an oven. The dried product was cracked into small granules and converted into H^+ form by treating with 1M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid 2 to 3 times. The excess acid was removed after several washings with DMW and finally dried at 50 °C. The particle size of approximately 125 μm of the composite cation-exchanger was obtained by sieving and stored in desiccators [19].

7.2.3 TEM (Transmission electron microscopy) studies

TEM studies were carried out to know the particle size of the poly-o-toluidine Zr(IV) phosphate composite cation-exchange material. From the TEM studies, it is clear that the poly-o-toluidine Zr(IV) phosphate cation-exchange material shows particle size range of 42.0 to 100.0 nm, thus the material particle size shows the nano-range.

7.2.4 Adsorption of Ziram on poly-o-toluidine Zr(IV) phosphate cation-exchanger

100 ml conical flask was taken for adsorption studies. In each flask, 25 ml Ziram solution (0.5-10 ppm) and 0.5g exchanger was taken. The flasks were closed and let them stand for 1 hour with intermittent shaking. Now, filter the contents and take 1ml of filtrate of each concentration in another conical flasks. In each flask add copper sulphate solution (1.0 mL), aqueous acetate buffer solution (1.0 mL, pH = 4.5) and Triton X-100 (2 mL), to make up the volume up to 10 mL with distilled water. The mixture was shaken vigorously for 2–3 min. The absorbance of the solution was measured at 437nm against a reagent blank [20].

The adsorption percentage (Ads %) from standard solution was calculated as:

$$Ads\ \% = {}^{C_o - C_e}\!/_{C_o} \times 100 \qquad \text{--------- 7.1}$$

Where C_o nd C_e are absorbance before and after adsorbed on cation-exchanger respectively. The adsorption percentage (Ads %) of Ziram before and after adsorption on poly-o-toluidine Zr(IV) phosphate cation-exchanger are given in Table 7.1.

Table 7.1 The adsorption percentage (Ads %) of Ziram before and after adsorption on poly-o-toluidine Zr(IV) phosphate cation-exchanger

S.No.	Concentration (ppm)	Initial Absorbance before adsorption	Absorbance after adsorption on poly-o-toluidine Zr(IV) phosphate cation-exchanger	Weight of adsorbent (g)	Ads %
1.	0.5	0.012	completely adsorbed	0.5	100
2.	0.6	0.016	completely adsorbed	0.5	100
3	0.8	0.018	completely adsorbed	0.5	100
4.	1.0	0.0229	0.001	0.5	95.6
5.	2.0	0.0592	0.019	0.5	84.7
6.	3.0	0.0732	0.015	0.5	79.5
7.	4.0	0.0976	0.022	0.5	77.5
8.	6.0	0.1472	0.036	0.5	75.5
9.	8.0	0.1995	0.055	0.5	72.4
10.	10	0.253	0.095	0.5	62.5

7.2.5 Absorption spectra

The absorption spectra of Ziram as copper(II) dimethyldithiocarbamate complex dissolved into Triton X-100 against a reagent blank and spectrum after adsorption on the cation-exchanger.

7.3 Preparation of Ziram pesticide sensitive membrane electrode

The ion-exchange membrane was prepared by following the procedure of Coetzee and Benson [21]. Poly-o-toluidine Zr(IV) phosphate cation-exchanger (100 mg) as electroactive material was ground to fine powder and was mixed thoroughly with Araldite (Ciba-Geigy, India Ltd.) (100 mg) in 1:1 (w/w) ratio to make a homogeneous paste, which was then spread between the folds of Whatman's filter paper No. 42. The phase of the exchanger and Araldite was kept under pressure of 2 kg cm^2 for 24 h and left to dry.

One sheet of thickness 0.14 mm of master membrane was prepared. This sheet was dipped in distilled water to remove filter paper. After drying, the membrane sheet was cut in the shape of disc using a sharp edge blade.

7.3.1 Fabrication of pesticide sensitive membrane electrode of poly-o-toluidine Zr(IV) phosphate cation-exchanger

The membrane electrode was fabricated as reported in the previous study [22]. The whole arrangement is shown below:

Internal reference electrode (SCE)	Internal electrolyte 0.1M Ziram	Membrane	Sample solution	External reference electrode (SCE)

Following parameters were evaluated to study the sensitivity of the electrode for the "Ziram " such as lower detection limit, electrode response curve and response time.

7.3.2 Electrode response or membrane potential

A series of Ziram solution of varying concentrations ranging from 10^{-1} M – 10^{-10} M were prepared. External electrode and pesticide selective membrane electrode are plugged in digital potentiometer and the potentials were recorded. First, the electrode was soaked in 1×10^{-1} M solution of Ziram for 2-3 days and for 1 hour before use. When electrode was not in use it must be kept in 1×10^{-1} M solution. Measured potential was plotted against selected concentration of the pesticide in solution.

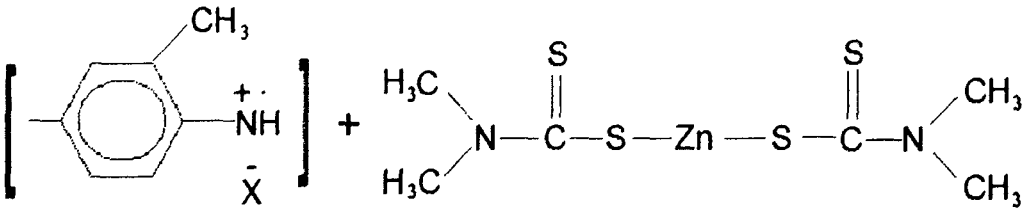
7.3.3 The response time

The electrode is first dipped in a 1×10^{-2} M solution of Ziram and then into 1×10^{-1} M concentration. The potential of the solution was read at zero second; just after dipping of the electrode in the second solution, the potential was recorded subsequently at the interval of 5 second. The potentials were then plotted vs. time.

7.4 Results and Discussion

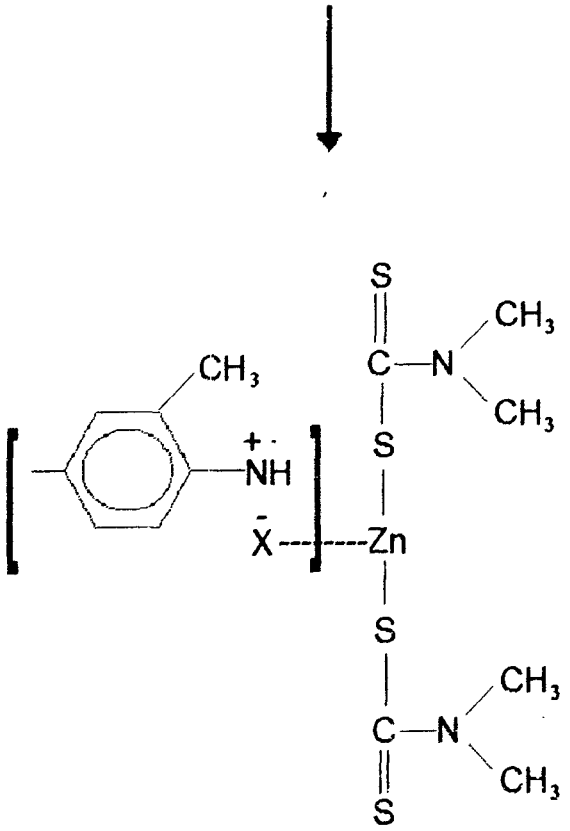
7.4.1 Adsorption of Ziram on poly-o-toluidine Zr(IV) phosphate composite

Poly-o-toluidine Zr(IV) phosphate is an presynthesized nano-composite cation-exchanger [19]. Its excellent ion exchange behavior is due to the presence of strong phosphate groups (co-ions) present in the matrix of the composite which have electrostatic attraction to positive cations (counter ions). Ziram, a Zinc based dimethyldithiocarbamate is adsorbed completely upto 0.8 ppm of the concentration and retain 60% of its adsorption upto 10 ppm (Table 7.1). The mechanism of adsorption can be represented by the following equation.



Poly-o-toluidine Zr(IV)phosphate where X is Zr(IV)phosphate

Zinc dimethyldithiocarbamate



Poly-o-toluidine Zr(IV) phosphate is formed by ionic interaction between the radical cation of poly-o-toluidine and anionic group of Zr(IV) phosphate. Phosphate groups of Zr(IV) phosphate behaves as co-ions for cation-exchange material and has an electrostatic potential for metal present in the carbamate pesticide. The adsorption of pesticide is too high due to the large surface area of the non-conventional adsorbent. As the adsorbent is nano-size (Figure 7.1), its surface area is higher in compare to the other adsorbent. However nano-particle size of the material (24.0 to 100 nm) as shown in increases the surface area of adsorbent, resulting maximum adsorption of pesticide.

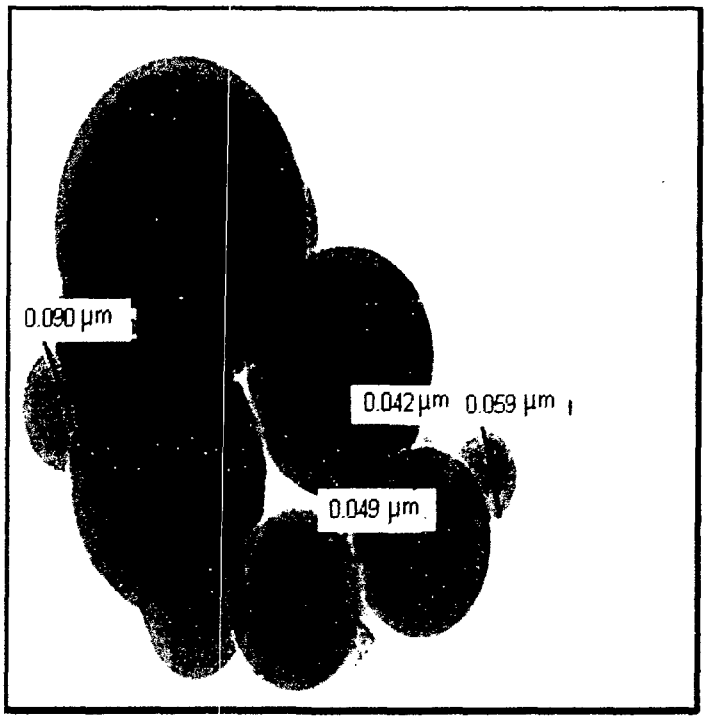


Figure 7.1 Transmission electron microscopy (TEM) shows the particle size of poly-o-toluidine Zr(IV) phosphate cation-exchange material

The absorption spectra of Ziram as copper(II) dimethyldithiocarbamate complex dissolved into Triton X-100 against a reagent blank and spectrum after adsorption on the cation-exchanger as shown in Figure 7.2. The absorbance of the solution was measured at 437nm against a reagent blank.

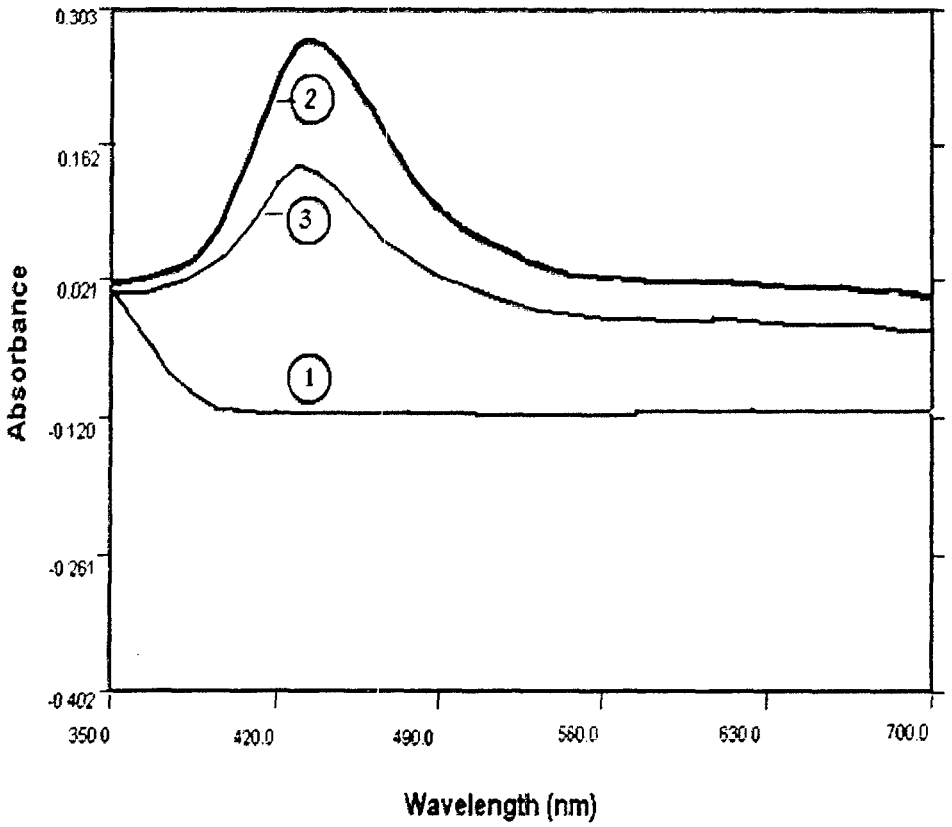


Figure 7.2 Absorption spectra of (1) blank solution, (2) Ziram-copper (II) dimethyldithiocarbamate complex in Triton X-100 against reagent blank before adsorption, (3) after adsorption of Ziram- copper (II) dimethyldithiocarbamate complex on poly-o-toluidine Zr(IV) phosphate cation-exchanger

Conditions: Ziram 10 ppm; copper sulphate 1.0 mL (1 g/L), acetate buffer 1.0 mL (pH 4.5)

7.4.2 Ziram sensitive membrane electrode

On the basis of the adsorption behavior of Ziram on the surface of Poly-o-toluidine Zr(IV) phosphate, the Ziram sensitive heterogeneous precipitate membrane electrode was prepared from poly-o-toluidine Zr(IV) phosphate cation-exchange material which gave linear response in the range 1×10^{-1} M - 1×10^{-7} M. The working concentration range is 1×10^{-1} M to 1×10^{-10} M (Figure 7.3) for Ziram with a lower Nernstian slope of 28.1 mV per decade change in Ziram concentration. The limit of detection determined from the intersection of the extrapolated segments of the calibration graph [23] was found to be 1×10^{-7} M.

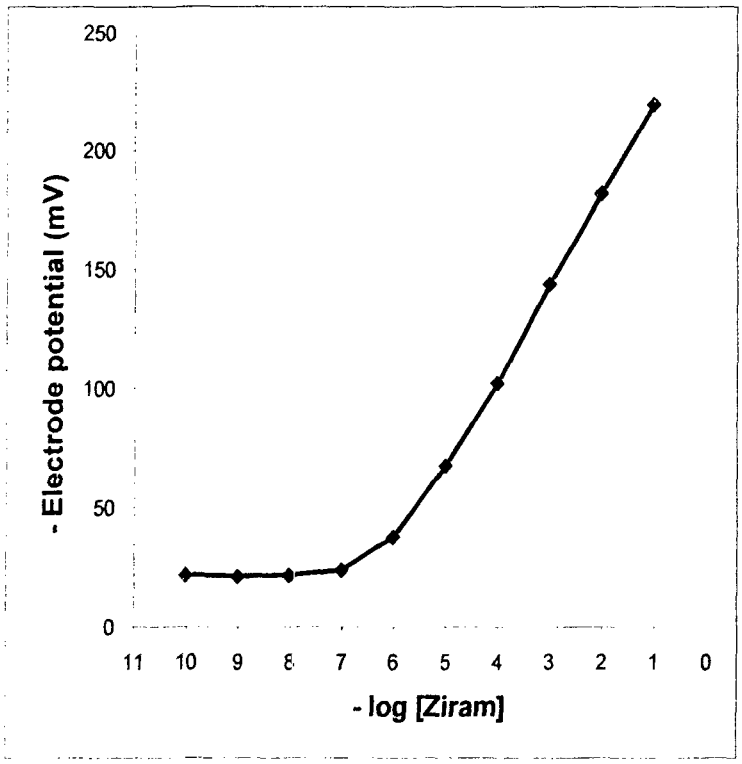


Figure 7.3 Calibration curve for Ziram sensitive membrane electrode

Promptness of the response of the pesticide sensitive electrode was also determined. The average response time is defined as the time required for the electrode to reach a stable potential. It is clear (Figure 7.4) that the response time of the membrane sensor is found to be ~ 45s. The membrane could be successfully used upto one month without any notable change in potential during which the potential slope is reproducible within ±1 mV per concentration decade. If a drift in the potential is observed, the membrane is re-equilibrated with 1×10^{-1}M solution for one week.

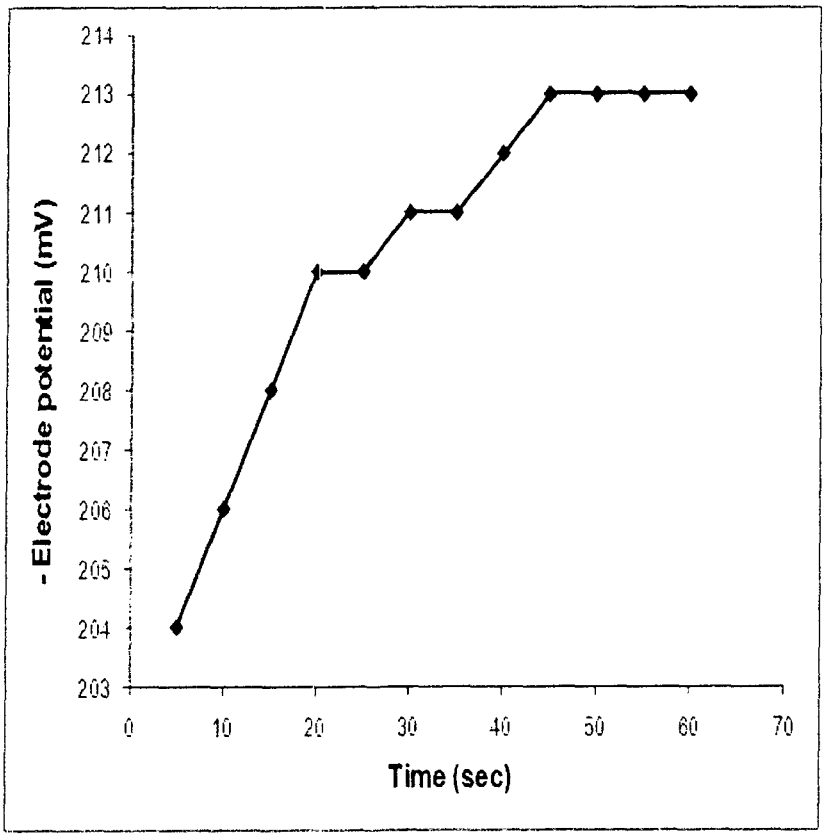


Figure 7.4 Time response curve of Ziram sensitive membrane electrode

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Chapter-8

Adsorption Thermodynamics studies of 2,4,5-Trichlorophenoxy acetic acid on Poly-o-toluidine Zr(IV) phosphate, a Nano-Composite Cation-exchanger: usedas Pesticide Sensitive Membrane Electrode

8.1 Introduction

The contamination of surface and ground water by pesticides is an important problem that the scientists are dealing with over the years. Pesticides are group of inorganic and organic compounds that may pollute water due to their extensive application in agriculture as rodenticides, insecticides, larvacides, miticides, mollucides, synergists, fumigants, fungicides, plant growth regulators and sterilants. Although much benefit is obtained from their uses, they have some undesirable side effects such as toxicity, carcinogenity and mutagenity [1,2].

2,4,5-trichlorophenoxy acetic acid (2,4,5-T) is used in forestry and in agriculture as a systemic herbicide. It is considered as moderately toxic and maximum allowable concentration in drinking water. On the other hand 2,4,5-T is a poorly biodegradable pollutant. Consequently, it has been frequently detected in water bodies in various regions of the world [3]. Therefore, the removal of pesticides from water is one of the major environmental concerns these days.

Several methods are available for pesticides removal such as photocatalytic degradation [4,5], combined photo-Fenton and biological oxidation [6], advanced oxidation processes [7], aerobic degradation [8], nanofiltration membranes [9], ozonation [10] and adsorption [11-19]. Adsorption on activated carbon is the most widespread technology used to deal with purification of water contaminated by pesticides [20], dyes [21-23] and phenols [24] etc.

It is interesting to use organic-inorganic composite materials in adsorption studies of pesticides [25-27]. Activated carbon, coal and bone char have been widely used in the adsorption of metal ions from aqueous solution. Adsorption behavior of some pesticides for the removal of heavy metals from aqueous solution and industrial wastewater has been reported by *Khan et al.* [28-32]. Such adsorption studies of pesticides on composite materials can help us in making pesticide sensitive membrane electrode that can be used to determine pesticide in trace amounts in the given sample of polluted water.

In the present study poly-o-toluidine Zr(IV) phosphate, a nano-composite cation-exchanger [33] is used for the adsorption studies of 2,4,5-T and some important thermodynamic parameters were also determined. On the basis of adsorption studies, a pesticide sensitive electrode was fabricated by using poly-o-toluidine Zr(IV) phosphate composite material.

Therefore, the purpose of this work was to evaluate the adsorption potential of poly-o-toluidine Zr(IV) phosphate cation-exchanger for 2,4,5-trichlorophenoxyacetic acid. The equilibrium data of the adsorption process were then studied to understand the adsorption mechanism of 2,4,5-T molecules onto the prepared cation-exchanger.

8.2 Experimental

8.2.1 Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-merck and Qualigens (India Ltd., used as received). Ortho-toluidine from CDH, 2,4,5-trichlorophenoxy acetic acid was obtained from Hindustan Ciba Geigy Ltd. (India). All other reagents and chemicals were of analytical grade. An electronic balance (digital, Sartorius-210S, Japan), an automatic temperature controlled water bath incubator shaker – Elcon (India) were used.

8.2.2 Preparation of reagents solution

0.1M solutions of Zirconium oxychloride ($ZrOCl_2.8H_2O$) and phosphoric acid (H_3PO_4) of different molarities were prepared in 4M HCl and demineralised water (DMW) respectively. Solutions of 20% (v/v) o-toluidine (C_7H_9N) and 0.4M Ammonium persulphate ($(NH_4)_2S_2O_8$) were prepared in 2M HCl.

The stock solution of 2,4,5-T (0.1M) was prepared in Ethanol. Different concentrations (10^{-1}M-10^{-12}M) of 2,4,5-T were prepared by diluting the stock solution with DMW. 0.1M Sodium hydroxide and phenolphthalein indicator.

8.2.3 Preparation of poly-o-toluidine Zr(1V) phosphate composite cation-exchange material (adsorbent)

The nano-composite cation-exchanger was prepared by the sol-gel mixing of poly-o-toluidine, an organic polymer, into the inorganic precipitate of zirconium(IV) phosphate. In this process, when the gels of poly-o-toluidine were added to the white inorganic precipitate of zirconium(IV) phosphate with a constant stirring, the resultant mixture were turned slowly into a greenish black colored slurries. The resultant greenish black colored slurries were kept for 24 hours at room temperature.

Now the poly-o-toluidine based composite gels were filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of ammonium persulphate. The washed gel dried over P_2O_5 at 40 °C in an oven. The dried product was

washed again with acetone to remove oligomers present in the material, and dried at 40 °C in an oven. The dried product was cracked into small granules and converted into H^+ form by treating with 1M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid 2 to 3 times. The excess acid was removed after poly-*o*-toluidine Zr(IV) phosphate several washings with DMW and finally dried at 50 °C. The particle size of approximately 125 μm of the composite cation-exchanger was obtained by sieving and stored in desiccators. Hence a number of nano-composite cation-exchange samples were prepared and on the basis of Na^+ ion exchange capacity (i.e.c.) that was found 1.71meq dry g^{-1} [33] was selected for further adsorption studies.

8.2.4 Characterization of adsorbent

8.2.4.1 SEM (Scanning Electron Microscopy) studies

Microphotographs of the original form of organic-inorganic composite material poly-o-toluidine Zr(IV) phosphate were obtained by Scanning Electron Microscopy EVO 50 at various magnifications and at different scale bar length.

8.2.4.2 TEM (Transmission Electron Microscopy) studies

TEM studies were carried out by Philips CM-10 Transmission Electron Microscope instrument to know the particle size of the poly-o-toluidine Zr(IV) phosphate composite cation-exchange material.

8.2.4.3 Characteristics of 2,4,5-trichlorophenoxy acetic acid

Origin/derivation: 2,4,5-T is produced synthetically by the reaction of 2,4,5-trichlorophenol, chloroacetic acid and sodium hydroxide. Lindane production residues are also useful for the 2,4,5-T synthesis.

Humans/mammals: 2,4,5-T considerably irritates the eyes, and the skin. Skin resorption is likely. Chronic exposure causes impairment of the liver function, changes in behaviour and nerve damage. 2,4,5-T is found to be slightly mutagenic and teratogenic. There are not enough facts to definitely attest cancerogenic effects.

Plants: 2,4,5-T is an effective defoliant. Plants (and in particular dicotyledons) absorb 2,4,5-T through their leaves and metabolise the substance. Numerous metabolic processes are impaired.

Environmental behaviour: There is moderate sorption of 2,4,5-T on organic suspended matter and on sediments. In soil, 2,4,5-T is either microbially degraded or it evaporates into the atmosphere.

Characteristics properties and toxicity or LD_{50} oral effects of 2,4,5-trichlorophenoxy acetic acid on different mammals are shown in Table 8.1 and Table 8.2.

Table 8.1 Characteristic properties of 2,4,5-trichlorophenoxy acetic acid

Empirical formula:	$C_8H_5Cl_3O_3$
Rel. molecular mass:	255.49 g
Density:	1.803 g/cm^3 at 20°C
Boiling point:	above 200°C decomposition
Melting point:	157-158°C (acid); 113-115°C (triethanolamine salt)
Vapour pressure:	0.7 x 10^{-6} Pa at 25°C
Solvolysis/solubility:	in water: 280 mg/l at 25°C in diethylether: 234 g/l; in toluene: 7.3 g/l; in xylene: 6.1 g/l; soluble in isopropyl alcohol; the alkali and amine salts of 2,4,5-T are readily soluble in water, whereas the esters are virtually insoluble in water but soluble in mineral oils

Table 8.2 Toxicity or LD_{50}, oral effect of 2,4,5-trichlorophenoxy acetic acid on some mammals and birds

Test Organism (Species/Sex)	LD_{50} (mg/kg)	Reference
Acute		
Mice	389	Hayes, 1982
Rat	300	Bailey and White, 1965
Rat	500	FAO, 2004; Hayes, 1982
Guinea pig	381	AAPCO, 1966; Hayes, 1982
Hamster	425	Grant, 1979
Dog	>100	FAO, 2004; Hayes, 1982

8.3 Equilibrium Studies

In 6 different 100ml conical flasks add different volumes of 2,4,5-T and water. Shake the solutions well and add 0.5g of adsorbent (poly-o-toluidine Zr(IV) phosphate) in each flasks. Stopper the flasks and let them stand for about 24 hours with intermittent shaking. Now, filter the contents and titrate it against N/10 sodium hydroxide solution using phenolphthalein as indicator. Take three readings in each case.

The adsorption percentage (Ads %) from standard solution was calculated as:

$$Ads\ \% = {}^{C_o - C_e}\!/_{C_o} \times 100 \qquad \text{---------8.1}$$

Where C_0 and C_e are initial and final concentrtion of 2,4,5-T respectively.

8.4 Fabrication of Pesticide Sensitive Membrane Electrode of Poly-o-toluidine Zr(IV) phosphate Cation-Exchanger

The membrane electrode was fabricated as reported in the previous study [34]. The whole arrangement is shown below:

Internal reference electrode (SCE)	Internal electrolyte 0.1M 2,4,5-T	Membrane	Sample solution	External reference electrode (SCE)

Following parameters were evaluated to study the sensitivity of the electrode for the "2,4,5-T" such as lower detection limit, electrode response curve and response time.

8.4.1 Electrode response or membrane potential

A series of 2,4,5-T solution of varying concentrations ranging from 10^{-1} M – 10^{-12} M were prepared. External electrode and pesticide selective membrane electrode are plugged in digital potentiometer and the potentials were recorded. First, the electrode was soaked in 1×10^{-4} M solution of 2,4,5-T for 2-3 days and for 1 hour before use. When electrode was not in use it must be kept in 1×10^{-4} M solution. Measured potential was plotted against selected concentration of the pesticide in solution.

8.4.2 The response time

The electrode is first dipped in a 1×10^{-4} M solution 2,4,5-T of and then into 1×10^{-3} M concentration. The potential of the solution was read at zero second; just after dipping of the electrode in the second solution, the potential was recorded subsequently at the interval of 5 second. The potentials were then plotted vs. time.

8.5 Results and Discussion

8.5.1 Characterization of adsorbent

SEM photograph of poly-o-toluidine Zr(IV) phosphate obtained at different magnifications (Figure 8.1) indicating the adhesion between two phases, i.e. inorganic ion-exchange material with organic polymer (poly-o-toluidine). The SEM pictures showed the difference in surface morphology of organic polymer, inorganic precipitate and composite material. It has been revealed that after binding of poly-o-toluidine with Zr(IV) phosphate, the morphology has been changed.

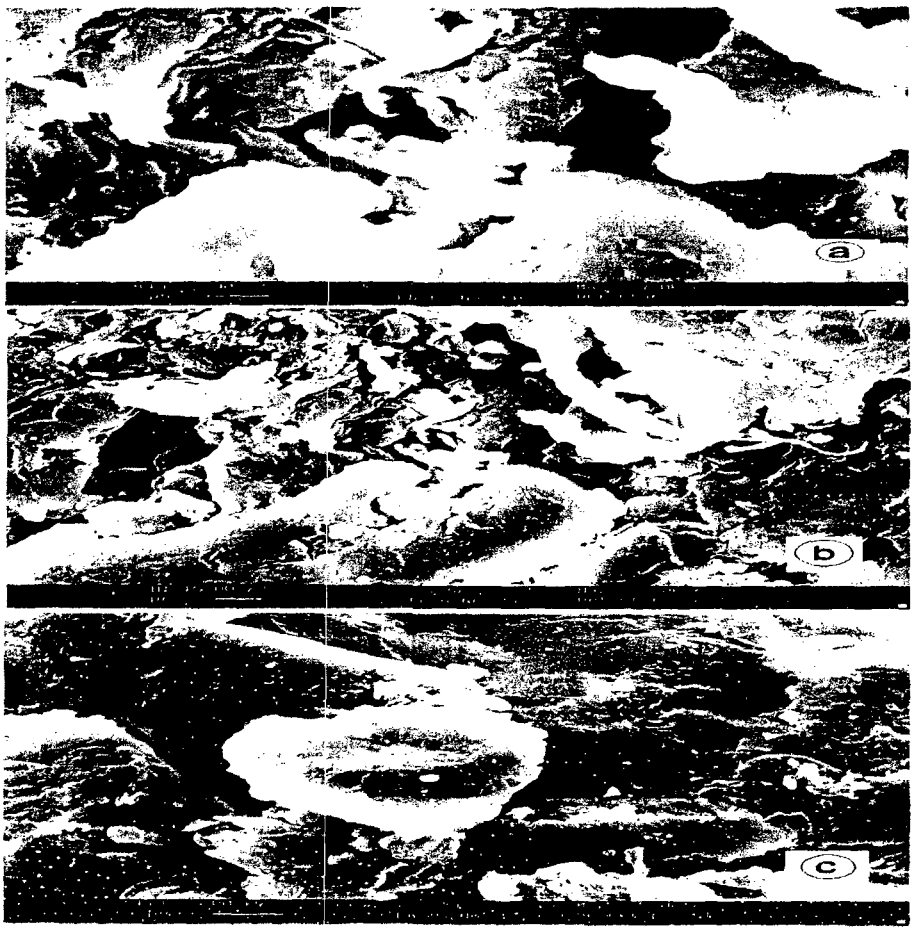

Figure 8.1 Scanning electron microphotographs (SEM) of chemically prepared poly-o-toluidine Zr(IV) phosphate composite system at different magnification and scale bar length of 1μm, 2μm and 3 μm

From the TEM studies, it is clear that the poly-o-toluidine Zr(IV) phosphate cation-exchange material shows particle size range of 42.0 to 100.0 nm, thus the material particle size shows the nano-range (Chapter-7, Figure 7.1).

8.5.2 Adsorption isotherms

The adsorption of 2,4,5-T on poly-o-toluidine Zr(IV) phosphate cation exchanger is represented by the adsorption isotherm. Out of the possible several isotherms equations, two have been applied for this study, the Freundlich and Langmuir isotherms.

At a given temperature, the mass of a solute (or gas) adsorbed by a solid adsorbent at various concentrations (pressure in case of gases) is given by the linear form of Freundlich equation [35] is expressed

$$q = x/m = K.\ C_e^{\ 1/n} \qquad \text{----------8.2}$$

In Eq. (8.2), x/m is the amount of 2,4,5-T adsorbed per unit weight of cation-exchanger (mg/g), Ce is the equilibrium concentration of 2,4,5-T (mg/L). Calculated and experimental q and C_e values obtained at different initial 2,4,5-trichlorophenoxy acetic acid concentrations are shown in Table 8.3.

Table 8.3 Calculated and experimental q and C_e values obtained at different initial 2,4,5-trichlorophenoxy acetic acid concentration

S.No.	Initial conc. of 2,4,5-T (C) in mg/L	Equil. conc. of 2,4,5-T after adsorption (C_e) in mg/L	Amount of 2,4,5-T adsorbed (x)	Weight of adsorbent (m) in gram	q = x/m (mg/g)	log q	log C_e	1/q	1/C_e
1.	0.1	0.086	0.3924	0.5	0.7849	-0.105	-1.066	1.274	11.628
2.	0.0833	0.0738	0.3368	0.5	0.6736	-0.172	-1.132	1.485	13.550
3.	0.0667	0.0617	0.2815	0.5	0.563	-0.250	-1.210	1.776	16.208
4.	0.05	0.042	0.1916	0.5	0.3832	-0.417	-1.377	2.610	23.810
5.	0.0333	0.0273	0.1246	0.5	0.2492	-0.604	-1.564	4.013	36.630
6.	0.01667	0.0137	0.0624	0.5	0.1248	-0.904	-1.863	8.013	72.993

K and n are constants with K is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the exponent, 1/n gives an indication of the favorability of adsorption [36,37]. K and n are Freundlich constants can be calculated from the linear plot of log q vs. log C_e as shown in Figure 8.2. The values of K and n can be determined from the intercept and slope, respectively of the logarithmic plot in Eq. 8.2.

$$\log q = \log K + 1/n \log C_e \qquad \text{-------8.3}$$

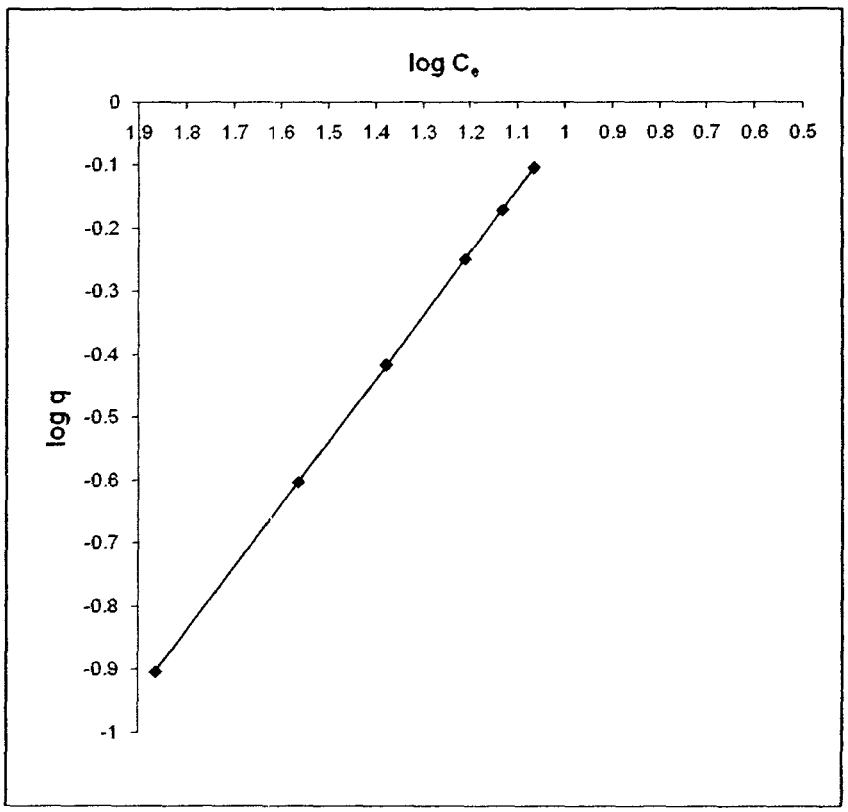

Figure 8.2 Freundlich adsorption isotherm for 2,4,5-trichlorophenoxy acetic acid on poly-o-toluidine Zr(IV) phosphate

The Langmuir adsorption model [38] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surfaces. The linear expression of the Langmuir model is given by Eq. (8.4)

$$q = abC_e/ (1 + bC_e) \qquad \text{-------8.4}$$

or its linear form

$$C_e/q = 1/ab + C_e/a \qquad \text{-------8.5}$$

where a and b are the Langmuir constants and related to the capacity and energy of adsorption respectively and can be determined from the slope and intercept of the 1/q vs $1/C_e$ linear plot (Figure 8.3). Using Langmuir constant (b), a dimensionless constant termed as separation factor R_L could be calculated according to Eq. (8.6)

$$R_L = 1/(1 + b\,C_0) \qquad \text{-------8.6}$$

where C_0 is the initial concentration of adsorbate in water. Depending on the values of R_L, the adsorption can be said favorable or unfavorable or irreversible. The values of R_L from 0 to 1 are favorable. When it is greater than 1 the adsorption is unfavorable and equals to zero signifies irreversible adsorption [39].

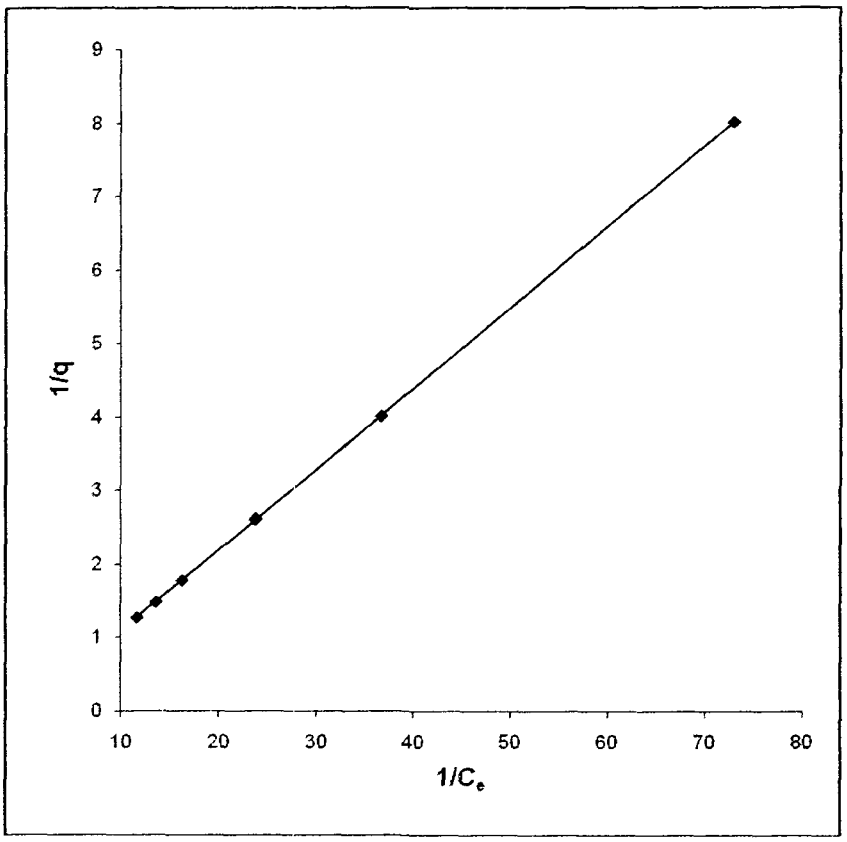

Figure 8.3 Langmuir adsorption isotherm of 2,4,5-trichlorophenoxy acetic acid on poly-o-toluidine Zr(IV) phosphate

From Figures 8.2 and 8.3, the values of constants a and b in Langmuir model and n and K in Freundlich model and the linear regression coefficients (R^2) had been calculated and are given in Table 8.4.

The values of constants a in Langmuir isotherm and K in Freundlich isotherm were 1.2 mg/g and 0.95 mg/g respectively and indicate appreciable adsorption of 2,4,5-T on the surface of cation-exchanger. The value of n was 1.0 and signifies favorable adsorption. The higher value of K_L calculated by Eq. (8.3) was 0.99 when the concentration of 2,4,5-T was taken 0.1 mg/L.

For 2,4,5-T, the values of a and b are found to be 1.2 mg/g and 0.1 l/mg (R^2 = 0.999) respectively and the values of K and n are found to be 0.95 mg/g and 1.0 (R^2 = 0.998) respectively. Thus the Freundlich equation becomes

$$q = 0.95\ C_e^{\ 1} \qquad \text{-------8.7}$$

and the Langmuir equation becomes

$$q = 0.12\ C_e/(1 + 0.1\ C_e) \qquad \text{-------8.8}$$

Table 8.4 Values of Langmuir and Freundlich constants and regression coefficients

Freundlich constants		**Langmuir constants**	
K (mg/g)	0.95	a (mg/g)	1.2
n	1.0	b (l/mg)	0.1
R^2	0.998	R^2	0.999

8.5.3 2,4,5-trichlorophenoxy acetic acid sensitive membrane electrode

The pesticide (2,4,5-T) sensitive heterogeneous precipitate membrane electrode obtained from poly-o-toluidine Zr(IV) phosphate cation-exchange material gave linear response in the range 1×10^{-1} M and 1×10^{-6} M. The working concentration range is 1×10^{-1} M to 1×10^{-9} M (Figure 8.4) for 2,4,5-T with a lower Nerstian slope of 20.13 mV per decade change in 2,4,5-T concentration. The limit of detection determined from the intersection of the extrapolated segments of the calibration graph [40] was found to be 1×10^{-6} M.

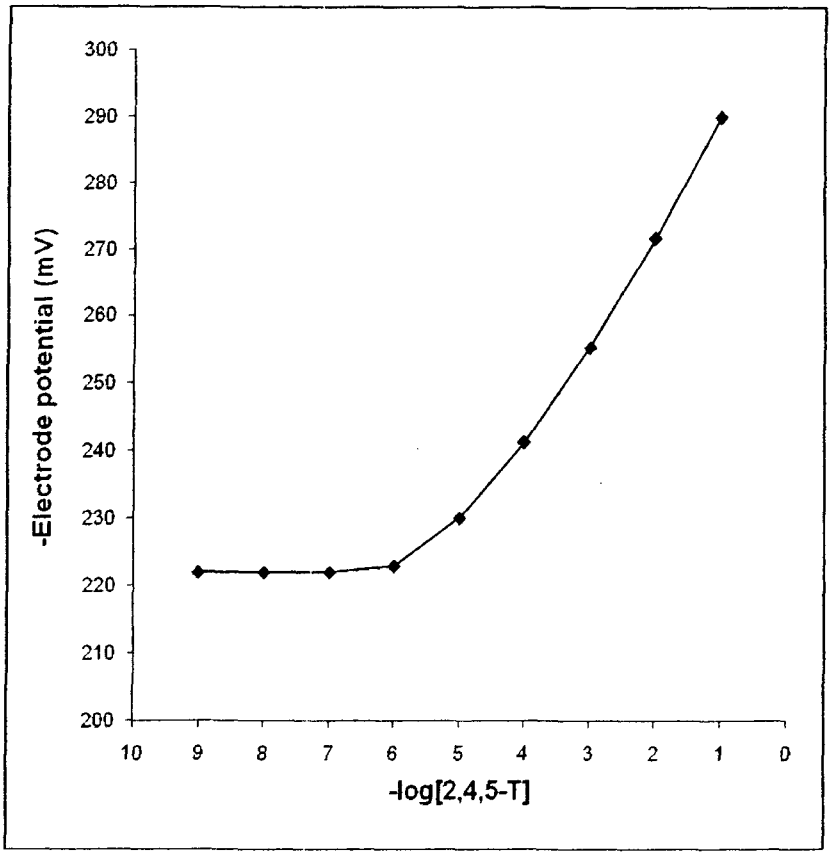

Figure 8.4 Calibration curve for 2,4,5- T sensitive membrane electrode in an aqueous solution

Promptness of the response of the pesticide sensitive electrode was also determined. The average response time is defined as the time required for the electrode to reach a stable potential. It is clear (Figure 8.5) that the response time of the membrane sensor is found to be ~15 s. The membrane could be successfully used upto one month without any notable change in potential during which the potential slope is reproducible within ±1 mV per concentration decade. If a drift in the potential is observed, the membrane is re-equilibrated with 1×10^{-3}M solution for one week.

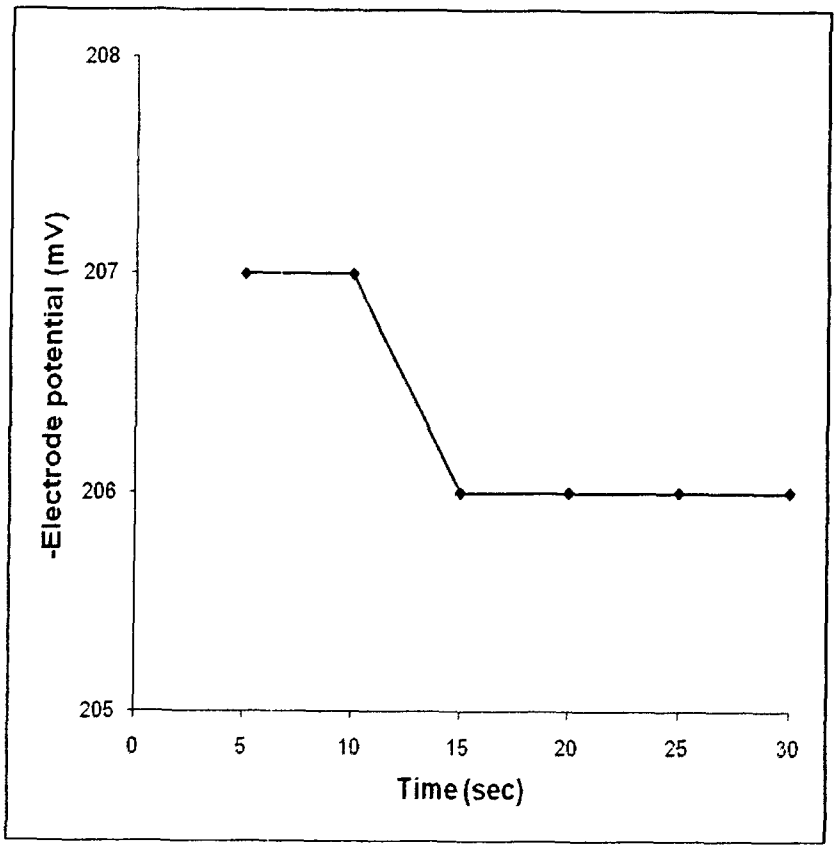

Figure 8.5 Time response curve of 2,4,5-T sensitive membrane electrode

8.6 Analytical Application

The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometeric titration of a 1×10^{-3} M Acetic acid and 1×10^{-3} M 2,4,5-T solution against 0.1M NaOH solutions as titrants. The results are shown in Figure 8.6. For this purpose, 5 ml portions of solutions were pippeted out in three different beakers, and the volume of each beaker was raised upto 20 ml by adding demineralized water. The solutions were titrated against 0.1M NaOH, the electrode potential was measured after each addition of 1.0 ml NaOH. The addition of titrants caused a decrease in the potential as a result of a decrease in the free ion concentration due to the neutralization of acid with base titrants. The amount of ions in solutions can be accurately determined from the resulting neat titration curves, providing a sharp end point.

Potentiometric titrations were also successfully carried out in the mixture of both 1×10^{-3} M Acetic acid and 1×10^{-3} M 2,4,5-T as shown in Figure 8.7. As pKa values for acetic acid and 2,4,5-T are 4.75 and 2.88 respectively, thus the end point of acetic acid

was obtained earlier than 2,4,5-T, hence demonstrating its applications as a sensor developed for the potentiometric determination of pesticide in mixtures. An unknown sample contained 2,4,5-T and the potentials were measured. The replicate measurements were made to obtain the pesticide concentration in the given sample with this electrode using the membrane sensor's calibration graph. The concentration of 2,4,5-T in the sample was ~ 10^{-3} M and the reproducibility of the results was checked up to three times.

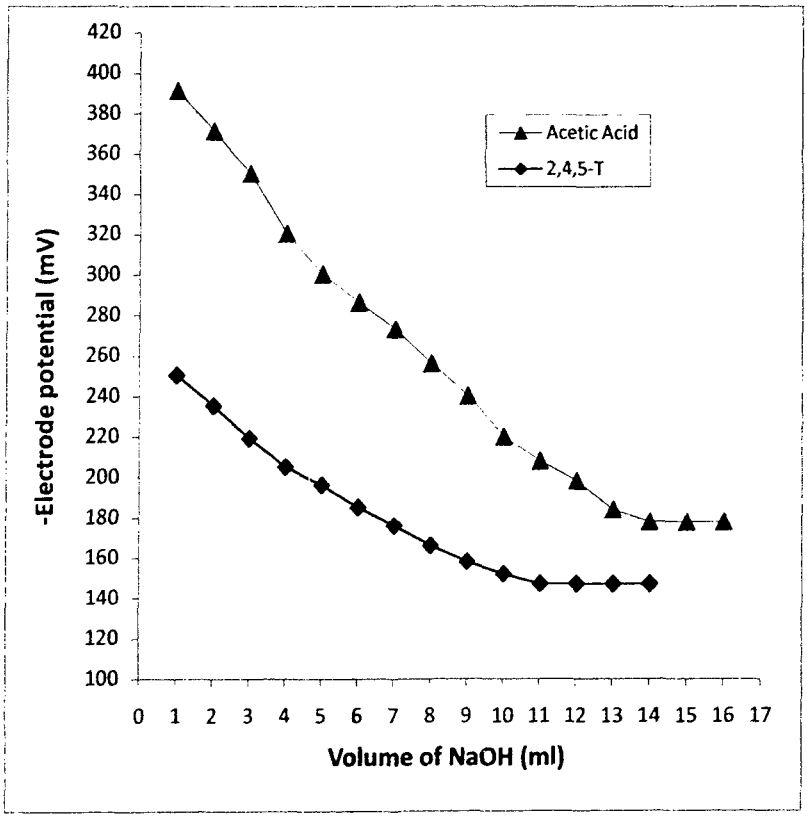

Figure 8.6 Potentiometeric titration against NaOH using 2,4,5-T sensitive membrane electrode

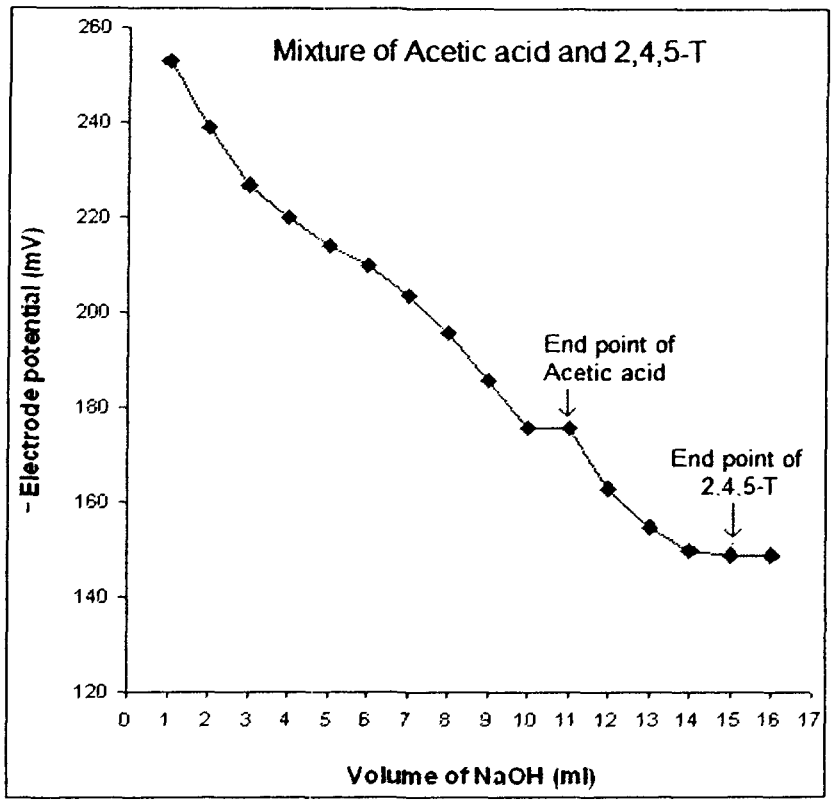

Figure 8.7 Potentiometeric titration of the mixture of Acetic acid and 2,4,5-T against NaOH using 2,4,5-T sensitive membrane electrode

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Appendix –I

Reprints of Publications

ANALYTICAL SCIENCES JULY 2008, VOL. 24

Organic-inorganic Composite Cation-exchanger: Poly-*o*-toluidine Zr(IV) Phosphate-based Ion-selective Membrane Electrode for the Potentiometric Determination of Mercury

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A new heterogeneous precipitate of an organic-inorganic composite cation-exchanger poly-*o*-toluidine Zr(IV) phosphate was utilized for the preparation of a Hg(II) ion-sensitive membrane electrode for the determination of Hg(II) ions in real aqueous as well as in real samples. The electrode showed good potentiometric response characteristics, and displayed a linear log[Hg^{2+}] *versus* EMF response over a wide concentration range of 1×10^{-1} - 1×10^{-6} M with a Nernstian slope of 30 mV per decade change in concentration with a detection limit of 1×10^{-6}. The membrane electrode showed a very fast response time of 5 s and could be operated well in the pH range 2 - 8. The selectivity coefficients were determined by the mixed-solution method, and revealed that the electrode was selective in the presence of interfering cations; however most of these did not show significant interference in the concentration range of 1×10^{-1} - 1×10^{-4} M. The lifetime of the membrane electrode was observed to be 120 days. The analytical utility of this electrode was established by employing it as an indicator electrode in the potentiometric titrations of Hg^{2+} ions from a synthetic mixture as well as drain water.

(Received May 22, 2007; Accepted October 29, 2007; Published July 10, 2008)

Ion-selective electrodes are among the important analytical tools, which are used for the sensitive and selective determination of various ionic species in the wide range of concentration[1] in environmental, medical and industrial samples.[2-4] Mercury is well-known for its toxicity, even in low concentration. Due to its toxicity, mercury causes ill effects in the human nervous system. Mercury also shows strong affinity for ligands containing S atoms, and thus causes the blocking of sulphydryl groups (-SH) of proteins, enzymes and membranes. Mercury(II) ions are also responsible for injuries of the kidney and gastrointestinal track. Due to its serious hazardous effects to human health, there is strong requirement to extend new methods to determine mercury ions in a wide variety of samples. Common methods are used to determine mercury, such as voltammetry,[5] spectrophotometry,[6,7] X-ray fluorescence,[8] flame and furnace atomic absorption spectrometry,[9,10] fluorometry,[11,12] cold vapor atomic absorption spectrometry[13] and inductively coupled plasma.[14] These methods, however, involve expensive instrumentation and sample pretreatment, which are time consuming and inconvenient. On the other hand, ion-selective membrane electrodes, commonly known as electrochemical sensors, are important in view of the ability to make direct or indirect measurements in complex samples without any knowledge about the color of the sample or the turbidity. The fact is that the use of ion-selective electrodes for such types of measurements requires relatively inexpensive equipment, which makes ion-selective electrodes attractive to scientists in many disciplines.[15] Thus, potentiometric sensors can offer an inexpensive and convenient method for the analysis of heavy-metal ions in solutions, providing acceptable sensitivity and selectivity. For this purpose many organic and inorganic compounds were studied as electroactive materials, and used in the fabrication of ion-selective membrane electrodes.[16-24] Composite materials are the latest development for making electrochemical sensors for analytical purposes.[25-30]

Poly-*o*-toluidine Zr(IV) phosphate, a composite cation-exchange material, was prepared by sol-gel mixing of organic polymer into the precipitate of Zr(IV) phosphate.[31] The composite material possess a better ion-exchange capacity (1.71 meq g^{-1}), as compared to Zr(IV) phosphate (1.46 meq g^{-1}). The presence of an organic component in the material prevents the leaching of any inorganic component in high acidic and alkaline media, and makes the material mechanically stable. These properties of composite materials helped us to make an ion-selective membrane electrode. In view of the above-mentioned facts in concerning the present study, we report on electroanalytical applications of organic-inorganic composite cation-exchanger poly-*o*-toluidine Zr(IV) phosphate as a Hg(II)-sensitive ion-selective membrane electrode.

Experimental

Reagents and instruments

The main reagents used for synthesizing the material were obtained from CDH, GSC, E-merck (India). All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India), a double-beam atomic-absorption spectrophotometer (GBC 902, Australia), a digital flame photometer (Elico CL 22D, India), a UV/Vis spectrophotometer (Elico EI 301E, India), a water-bath incubator shaker, and a digital potentiometer (Equiptronics EQ 609, India) with a saturated calomel electrode as a reference electrode were used.

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Table 1 Conditions of the preparation and the ion-exchange capacity of a poly-*o*-toluidine Zr(IV) phosphate composite cation-exchange material

Sample	Mixing volume ratio (v/v)					Appearance of beads after drying	Na^+ ion-exchange capacity/meq dry g^{-1}
	0.1 M $ZrOCl_2 \cdot 8H_2O$ in 4 M HCl	3 M H_3PO_4 in DMW	pH of the inorganic precipitate	0.4 M $K_2S_2O_8$ in 2 M HCl	20% *o*-toluidine in 2 M HCl		
S-1	1	2	1	1	1	Greenish granular	1.71
S-2	1	2	1	—	—	White granular	1.46

Preparation of poly-o-toluidine Zr(IV) phosphate organic-inorganic composite cation-exchange material

Poly-*o*-toluidine Zr(IV) phosphate, a composite cation-exchanger, was prepared as reported in our earlier study.[34] An organic polymer derivative of polyaniline, which is the poly-*o*-toluidine, was prepared by mixing in similar volume ratios of a solution of 0.4 M ammonium persulfate ($(NH_4)_2S_2O_8$) prepared in 4 M HCl into 20% *o*-toluidine (C_7H_9N), prepared in 2 M HCl with continuous stirring by a magnetic stirrer for 2 h at 0°C; a green-colored gel was obtained. The gel was kept for 24 h at 0°C. After that, the gel was transferred into the white precipitate of an inorganic ion-exchanger Zr(IV) phosphate, prepared at room temperature (25 ± 2°C) and at pH 2 by adding a 1:2 volume ratio of 0.1 M zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) prepared in 4 M HCl to an aqueous solution of 3 M *o*-phosphoric acid (H_3PO_4). The green-colored product gel was left for 24 h at room temperature for digestion. At the final stage, the composite cation-exchanger gel was filtered off, and washed with demineralized water (DMW) to remove excess acid. The washed gel was dried over P_4O_{10} at 40°C in an oven. The dried product was washed again with acetone to remove any oligomers present in the material, and dried at 40°C in an oven. The dried product was cracked into small granules and converted into H^+ form by treating with 1 M HNO_3 for 24 h with occasional shaking, intermittently replacing the supernatant liquid with fresh acid 2 to 3 times. The excess acid was removed after several washings with DMW, and finally dried at 50°C. A particle size of approximately 125 μm of the composite cation-exchanger was obtained by sieving and storing in desiccators. The composite cation-exchanger having maximum capacity (1.71 meq dry g^{-1}), as compared to Zr(IV) phosphate (1.46 meq dry g^{-1}), was selected for detailed studies of ion-selective electrode preparation. The condition of preparation and the ion-exchange capacity and physical appearance of the composite cation-exchanger poly-*o*-toluidine Zr(IV) phosphate (sample S-1) are given in Table 1.

Distribution (sorption) studies

The distribution coefficients (K_d values) of various metal ions on poly-*o*-toluidine Zr(IV) phosphate were determined by a batch method in various solvent systems. Various 0.2 g portions of the composite cation-exchanger beads (S-1) in the H^+-form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium, and kept for 24 h with continuous shaking for 6 h in a temperature-controlled incubator shaker at 25 ± 2°C to attain equilibrium. The initial metal ion concentration was adjusted so that it would not exceed 3% of its total ion-exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against a standard 0.005 M solution of EDTA.[32] The alkali metal ions, K^+, Na^+, Ca^{2+}, were determined by flame photometry, and some heavy metal ions, such as Pb^{2+}, Hg^{2+}, Zn^{2+}, were determined by atomic absorption spectrophotometry (AAS). The distribution coefficient (K_d) values were calculated by using the formula given below:

$$K_d = \frac{\text{mmol of metal ions/g of ion-exchanger}}{\text{mmol of metal ions/ml of solution}} \text{ (ml g}^{-1}\text{)}, \quad (1)$$

$$i.e.\ K_d = [(I - F)/F] \times (V/M) \text{ (ml g}^{-1}\text{)}, \quad (2)$$

where I is the initial amount of the metal ion in the solution phase, and F is the final amount of the metal ion in the solution phase. V is the volume of the solution (ml) and M is the amount of the exchanger (g).

Preparation of poly-o-toluidine Zr(IV) phosphate composite cation-exchanger membrane

A composite cation-exchange membrane was prepared by adaptating the method of Coetzee and Banson.[33] The poly-*o*-toluidine Zr(IV) phosphate cation-exchange material as an electroactive component for preparing the membrane was ground to fine powder, and thoroughly mixed with different amounts of PVC dissolved in 10 ml of tetrahydrofuran (THF), and finally mixed with 10 drops of dioctylphthalate, used as a plastisizer.[34] The mixing ratio of the ion-exchange was varied with a fixed ratio of PVC for the purpose of obtaining a composition, which gave a membrane showing the best performance. The resulting solutions were carefully poured into a glass casting ring (diameter 10 mm) resting on a glass plate. These rings were left for slow evaporation of THF to obtain thin films. In this way, 4 sheets of different thicknesses of the master membranes were obtained.

Characterization of membrane

The pre-requisite performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters were the membrane water content, porosity, thickness, swelling, *etc.* and were determined as described elsewhere,[35-38] after conditioning the membrane, as given below.

Conditioning of the membrane

The membranes were conditioned by equilibrating with 1 M sodium chloride; about 1 ml of sodium acetate was also added to adjust the pH to 5 - 6.5 (to neutralize the acid present in the film).

Water content (% total wet weight)

The conditioned membranes were first soaked in water to elute any diffusible salts, blotted quickly with Whatman filter paper to remove surface moisture, and immediately weighed. These were further dried to a constant weight in a vacuum over P_4O_{10} for 24 h. The water content (% total wet weight) was calculated as

Table 2 Characterization of an ion-exchanger membrane

Sample	Membrane composition			Thickness/ mm	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
	Poly-*o*-toluidine Zr(IV) phosphate/mg	PVC/ mg	Plasticizer/ drops				
M-1	100	200	10	0.14	1.89	0.200	0.1
M-2	200	200	10	0.20	2.27	0.214	0.2
M-3	400	200	10	0.32	3.89	0.244	0.4
M-4	600	200	10	0.64	4.48	0.360	0.4

$$\% \text{ Total wet weight} = \frac{W_w - W_d}{W_w} \times 100, \quad (3)$$

where W_w is the weight of the soaked/wet membrane and W_d is the weight of the dry membrane.

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data,

$$\varepsilon = \frac{W_w - W_d}{AL\rho_w} \quad (4)$$

where A is the area of the membrane. L is the thickness of the membrane and ρ_w is the density of water.

Thickness and swelling

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze.

Swelling was measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane. The results of the membrane characterization are given in Table 2.

Fabrication of ion-selective electrode

A membrane sheet (M-1) of 0.14 mm thickness, obtained by the above procedure, was cut in the shape of a disc and mounted at the lower end of a Pyrex glass tube (o.d. 1.6 cm, i.d. 0.8 cm) with Araldite. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with a 0.1 M mercuric nitrate $Hg(NO_3)_2$ solution. A saturated calomel electrode was inserted in the tube for electrical contact, and another saturated calomel electrode was used as an external reference electrode. The whole arrangement can be shown as follows:

Internal reference electrode (SCE) | Internal electrolyte 0.1 M Hg^{2+} | Membrane | Sample solution | External reference electrode (SCE)

Potential measurement and calibration

The performance of the response of the electrode in terms of the electrode potential (at 25 ± 2°C), corresponding to the concentration of a series of standard solutions of $Hg(NO_3)_2$ (10^{-9} - 10^{-1} M), prepared by serial dilution, was determined at a constant ionic strength, as described by IUPAC Commission for Analytical Nomenclature.[39] The membrane electrode was conditioned by soaking in a 0.1 M $Hg(NO_3)_2$ solution for 2 days and 1 h for at least before use. The experiments were conducted in air, maintained at 25 ± 1°C by a thermostat. After performing, the experimental membrane electrode was removed from the test-solution and kept in a 0.1 M $Hg(NO_3)_2$ solution.

The data concerning the measured potential of the membrane electrode were plotted against selected concentrations of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system. In order to study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time and working pH range.

The response time was measured by recording the e.m.f. of the electrode as a function of time when it was immersed in the solution to be studied. The electrode was usually first dipped in a 1×10^{-3} M solution of the ion concerned, and immediately shifted to another solution (pH ~4.0) of 1×10^{-2} M ion concentration of the same ion (10 fold higher concentration). The potential of the solution was read at zero second, that is, just after immediate dipping of the electrode in the second solution, and subsequently recorded at intervals of 5 s. The potentials were then plotted against time. The time during which the potentials attained a constant value represents the response time of the electrode.

A series of solutions of varying pH in the range of 1 to 14 were prepared, while keeping the concentration of the relevant ion constant (1×10^{-3} M). The pH variations were brought out by the addition of dilute acid (HCl) or dilute alkali (NaOH) solutions. The value of the electrode potential at each pH was recorded, and plotted against the pH.

To study the cationic interference due to other ions, the selectivity coefficients of various interfering cations for the ion-selective membrane electrode were determined by the mixed-solution method, as discussed elsewhere.[40] A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-3} M) and varying concentrations (1×10^{-1} - 1×10^{-9} M) of the primary ion. The potential measurements were then made by using the membrane electrode assembly.

Storage of membrane electrode

An ion-selective membrane electrode prepared by poly-*o*-toluidine Zr(IV) phosphate was stored in distilled water when not in use for more than one day. The electrode was activated with a 0.1 M $Hg(NO_3)_2$ solution by keeping it immersed in the solution for 1 h, before use, to reimburse for any loss of metal ions that might have been taken place due to long storage in demineralized water (DMW). The electrode was then thoroughly washed with DMW before use.

Results and Discussion

The composite material poly-*o*-toluidine Zr(IV) phosphate was prepared by the incorporation of a derivative of polyaniline *i.e.* poly-*o*-toluidine, into the matrices of inorganic cation-exchanger Zr(IV) phosphate. It is clear from Table 1 that the composite cation-exchanger possessed a better Na^+ ion-exchange capacity

Table 3 K_d-values of some metal ions on a poly-*o*-toluidine Zr(IV) phosphate column in different solvent systems

Metal ion	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12	S-13
Pb^{2+}	116	40	55	40	50	38	81	114	114	54	116	200	16
Hg^{2+}	476	—	—	715	433	—	130	—	585	520	1560	357	1820
Cu^{2+}	200	11	16	12	75	13	—	6	233	166	233	233	45
Co^{2+}	67	5	25	16	66	24	59	59	100	66	47	66	63
Cd^{2+}	157	54	60	30	60	—	—	—	200	172	133	325	233
Zn^{2+}	1900	23	45	31	23	—	—	—	100	114	100	172	100
Ni^{2+}	60	25	77	133	175	60	30	55	200	60	50	150	60
Mn^{2+}	150	—	100	100	350	—	—	—	200	200	22	—	150
Fe^{2+}	233	275	66	300	42	150	166	200	225	66	125	100	400
Al^{2+}	44	200	60	400	45	66	233	133	23	60	114	40	150

S-1, DMW; S-2, 0.1 M HCl; S-3, 0.01 M HCl; S-4, 0.1 M HNO_3; S-5, 0.01 M HNO_3; S-6, 10% formic acid; S-7, 20% formic acid; S-8, 30% formic acid; S-9, 10% ethanol; S-10, 20% ethanol; S-11, 10% acetone; S-12, buffer pH 3.75; S-13, buffer pH 5.75.

(1.71 meq dry g^{-1}) as compared to Zr(IV) phosphate (1.46 meq dry g^{-1}). Distribution studies of 12 metal ions were achieved in different solvent systems to realize the selective nature of this composite material (S-1) for fabricating a heterogeneous ion-selective membrane electrode. The distribution studies (Table 3) showed that the K_d values varied with the nature and the composition of the contacting solvents. It was also observed from sorption studies (K_d values) that the composite had a maximum selectivity towards Hg^{2+}, because mercury was highly adsorbed in all solvents, while the remaining metal ions were poorly adsorbed. The adsorption and ion-selective properties of this composite cation-exchanger may be confirmed by the high uptake of mercury ions in all solvents. On this basis, the composite cation-exchanger was used as an electroactive component in the preparation of a heterogeneous ion-selective membrane electrode sensitive to Hg(II) ions.

Preliminary experiments were carried out to find an optimum membrane composition of good electrochemical performance for fabricating the electrode. The optimized membrane was then used to test the performance of the membrane electrode. Therefore, four samples of poly-*o*-toluidine Zr(IV) phosphate cation-selective membranes were prepared using different mixing ratios of poly-*o*-toluidine Zr(IV) phosphate as an electroactive material, and PVC as a binder dissolved in tetrahydrofuran (THF) with a fixed amount (10 drops) of plasticizer dioctylphthalate. The amount of the ion-exchanger was varied so as to change the thickness of the membranes coating. The results are given in Table 2. It was observed that as the amount of electroactive component of the membrane *i.e.* poly-*o*-toluidine Zr(IV) phosphate increased, the thickness, swelling, water content, porosity increased. Thus, the low orders of water content, swelling and porosity with less thickness of this membrane suggest that the interstices are negligible and diffusion across the membrane would occur mainly through the exchange sites. Hence, membrane sample M-1 (thickness 0.14 mm) was selected for the preparation of an ion-selective electrode for further studies. However, further various characteristics are necessary for a membrane ion-selective electrode to be considered as a suitable sensor for the quantitative measurement of ions. The most important characteristics are the slope, working concentration range, response time, pH, selectivity and life span of the membrane electrode.

The potentiometric response of the membrane electrode prepared from membrane sample M-1 over a wide concentration range 10^{-1} - 10^{-9} is shown in Fig. 1. The electrode showed a linear Nernstian response for Hg(II) ions in the concentration range 1×10^{-1} - 1×10^{-6} M with an over Nernstian slope of 30

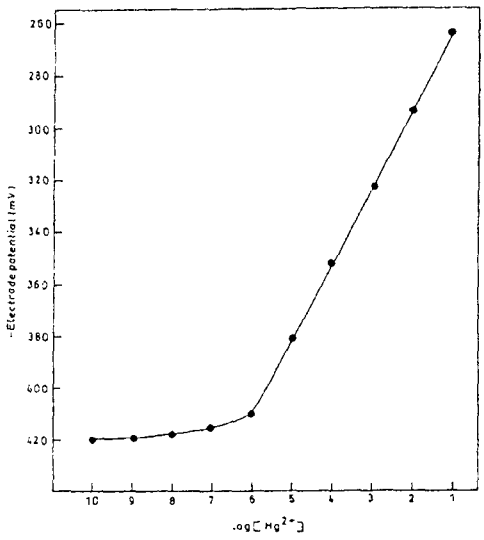

Fig. 1 Calibration curve for a poly-*o*-toluidine Zr(IV) phosphate membrane electrode in an aqueous solution of $Hg(NO_3)_2$.

mV per decade change in concentration. The limit of detection of the electrode, as determined according to the IUPAC recommendation[41,42] form the intersection of two segments of calibration curve, was 1×10^{-6} M. An over-Nernstian response in electrode of this kind is common.[43-45]

A calibration curve was made by measuring the electrode response to standard solutions prepared by serial dilution without the addition of extra indifferent salts. The ionic strength will increase linearly with an increase in the concentration. This would lead to a gradual decrease of the activity coefficient; the calibration curve (E *vs.* log(concentration)) showed a negative deviation from the straight line for concentrations above 10^{-3} - 10^{-2} M. This curvature of the calibration curve can be precluded by working at a constant ionic strength. This is commonly achieved by adding a large excess of an indifferent electrolyte, the ionic strength buffer.

It was observed that the response time of the poly-*o*-toluidine Zr(IV) phosphate membrane electrode was 5 s, according to the IUPAC recommendations,[46] to reach a potential within ±2 mV of its final equilibrium value. Although solid contact electrodes are often criticized for their poor response and stability, the response of this electrode is quick, and the lifetime is

Table 4 Comparison of the response characteristics of different Hg^{2+} ion-selective electrodes

Sample	Working concentration range/M	Lifetime	pH range	Response time	Slope (mV decade^{-1})	Ref.
1	$1 \times 10^{-1} - 1 \times 10^{-6}$	2 months	1.0 - 3.0	30 s	29	47
2	$1 \times 10^{-1} - 1 \times 10^{-5}$	4 months	2 - 4	6 min	30 - 32	48
			6 - 8		48	
3	$1 \times 10^{-1} - 1 \times 10^{-5}$	5 weeks	1.0	4 min	Not mentioned	49
4	$1 \times 10^{-1} - 1 \times 10^{-5}$	5 weeks	0 - 2.0	Less than 3 min	28.5	50
5	$1 \times 10^{-1} - 1 \times 10^{-5}$	3 months	2.8 - 3.9	30 - 40 s	29.0	51
7	$1 \times 10^{-1} - 1 \times 10^{-6}$	2 months	Not mentioned	20 - 100 s	28.6	52
8	$1 \times 10^{-1} - 1.41 \times 10^{-6}$	4 months	2 5 - 5.0	18	30	53
9	$5 \times 10^{-2} - 7.5 \times 10^{-6}$	Not	6 5	20 s	61.1	54
	$1 \times 10^{-2} - 5 \times 10^{-6}$	mentioned	4.0		28.7	
10	$1 \times 10^{-1} - 5 \times 10^{-5}$	3 months	1.3 - 4.0	20 s	27.3	55
11	$1 \times 10^{-1} - 1 \times 10^{-6}$	3 months	2 - 8	5 s	30	Proposed assembly

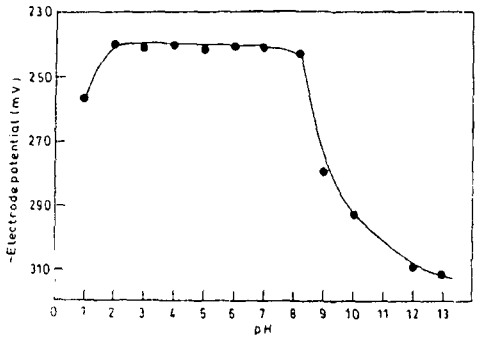

Fig. 2 Effect of the pH on the electrode response of Hg^{2+} ion-selective poly-*o*-toluidine Zr(IV) phosphate membrane electrode.

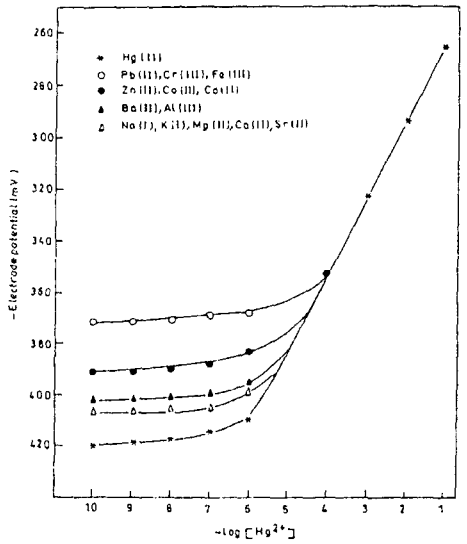

Fig. 3 Selectivity coefficients of various interfering ions for a poly-*o*-toluidine Zr(IV) phosphate membrane electrode.

reasonable, at least for 3 months. It is very important that the performance of any ion-selective electrode should be checked soon every time before using it for any analytical purpose. For the present poly-*o*-toluidine Zr(IV) phosphate membrane electrode, it was observed that the measured potential of Hg^{2+} ions in a given concentration range of $10^{-1} - 10^{-9}$ M was reproducible within ±2 mV, and there was no significant change in the slope of the Nernst plot during the experiment over a time period of 3 months. This suggests a longer electrode life and a stable electrode performance.

A comparison of the present Hg^{2+}-ISEs with those already reported in the literature is given in Table 4. From Table 4, it is clear that the performance of the proposed Hg(II) ion-selective membrane electrode based on the organic-inorganic composite cation-exchanger polyaniline Sn(IV) phosphate is comparable, and even better in many respects, such as the slope, response time, linear concentration range, lifetime, pH range and selectivity. It is clear from Fig. 2 that the pH influenced the response characteristics of the proposed Hg(II) ion-selective membrane electrode: that the potential remained unchanged within the pH range 2 - 8. After that pH, the electrode behaved in an erratic manner, which may be because mercury ions formed a hydroxyl complex and precipitated. Thus, we can say that the optimum pH range of operation of this electrode was pH 4 - 7.

The selectivity of the composite cation-exchanger is dependent on the distribution coefficient pattern, while that of for the electrode is upon the potentiometric selectivity coefficient values. Thus, the selectivity of the membrane electrode is one of the most important characteristics, which is a measure of its response for the primary ion in the presence of other ions, *i.e.* interfering ions. The selectivity of the electrode is determined in terms of potentiometric selectivity coefficient, $K^{POT}_{Hg,M}$, by mixed solution methods.[44] The selectivity coefficients of various cations for the Hg(II) ion-selective poly-*o*-toluidine Zr(IV) phosphate membrane electrode at pH 4 were determined, and form Fig. 3 and the results are summarized in Table 5.

The selectivity coefficients of bivalent and trivalent metal ions, like Co(II), Zn(II), Cd(II), Pb(II), Ba(II), Cr(III), Fe(III) and Al(III), showed somewhat higher values and interfered to a very little extent. However, Ba(II), Mg(II), Ca(II), Sr(II) and Al(III) showed very low selectivity coefficients, and hence interference was found to be negligible. However, the values of the selectivity coefficients in case of monovalent cations, like Na(I) and K(I), are exceptionally high due to the smaller charge of the interfering ions. Therefore, despite their large selectivity coefficients, these ions would not disturb the functioning of the Hg(II)-selective membrane electrode. Thus, the results revealed that the electrode was selective for Hg(II) in the presence of interfering cations. Therefore, it is understandable the poly-*o*-toluidine Zr(IV) phosphate interacts relatively strongly with Hg(II) ions, and can be successfully used as a sensing agent for mercury-selective electrodes.

Table 5 Selectivity coefficients, $K^{POT}_{Hg,M}$, of various interfering ions (M^{n+})

M^{n+}	$K^{POT}_{Hg,M}$	M^{n+}	$K^{POT}_{Hg,M}$
Pb^{2+}	1×10^{-1}	Al^{3+}	1×10^{-3}
Cr^{3+}	1×10^{-2}	Na^{+}	5.5
Fe^{3+}	1×10^{-2}	K^{+}	5.5
Zn^{2+}	5×10^{-2}	Mg^{2+}	5.5×10^{-3}
Co^{2+}	5×10^{-2}	Ca^{2+}	5.45×10^{-3}
Cd^{2+}	5×10^{-2}	Sr^{2+}	5.45×10^{-3}
Ba^{2+}	1×10^{-2}		

Analytical application

The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometeric titration of a 0.01 M $Hg(NO_3)_2$ solution against EDTA, oxalic acid and potassium dichromate solutions as titrants. The results are shown in Fig. 4. For this purpose, 5 ml portions of $Hg(NO_3)_2$ solutions were pippeted out in three different beakers, and the volume of each beaker was raised up to 20 ml by adding demineralized water. The solutions were titrated against EDTA, oxalic acid and potassium dichromate solutions respectively; the electrode potential was measured after each addition of 0.5 ml. The necessary adjustment of pH (~4) was made before adding the titrant. The addition of titrants caused a decrease in the potential as a result of a decrease in the free Hg(II) ion concentration due to the formation of a complex with titrants. The amount of Hg(II) ions in solutions can be accurately determined from the resulting neat titration curves, providing a sharp end point. Potentiometric titrations of Hg(II) were also successfully carried out in the presence of 1×10^{-5} M Ni(II), Cu(II) and Zn(II), hence demonstrating its applications as a sensor developed for the potentiometric determination of Hg(II) in mixtures. Poly-*o*-toluidine Zr(IV) phosphate, Hg^{2+} ion-selective membrane electrodes were also applied to direct measurements of Hg^{2+} in the drain water collected from Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India. The samples were collected by a routine technique from five different locations of drains, and preserved with HNO_3, stored in glass bottles and analyzed within 12 h after collection. Since the samples contained particulate matters, they were centrifuged, and the potentials were measured after adjusting the pH to ~4 with HNO_3 or NH_3. Three replicate measurements were made to obtain the Hg(II) contents in five samples with this electrode using the membrane sensor's calibration graph. The concentration of mercury in the sample was 10^{-3} M, and the reproducibility of the results was checked up to three times.

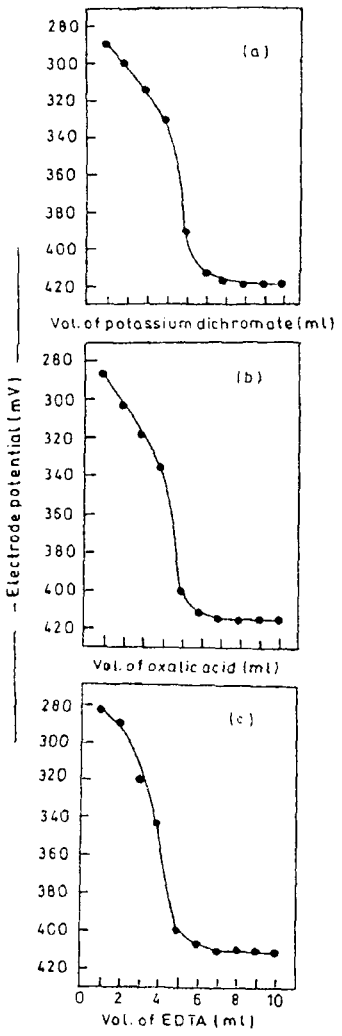

Fig. 4 Potentiometric titration of Hg(II) against (a) potassium dichromate, (b) oxalic acid, and (c) EDTA solutions.

Conclusions

An organic-inorganic composite cation-exchanger based PVC membrane electrode was found to be selective and sensitive for Hg(II) ions. The membrane electrode possessed a quick response time of only 5 s, and the functional pH range of the electrode was 2 - 8 with a slope of 30 mV per decade change in the concentration range of 1×10^{-1} - 1×10^{-6} M. The selectivity of the ion-selective electrode was good over a wide range of interfering metal ions. It showed a good reproducibility detection limit and a lifetime of 3 months. It could be successfully applied in the potentiometric titration of Hg(II) ions in solution with EDTA, oxalic acid and potassium dichromate in the presence of metal nitrate solutions.

Acknowledgements

The authors are thankful to Department of Applied Chemistry, Z. H. College of Engineering and Technology, A.M.U. (Aligarh) for providing research facilities and Council of Scientific and Industrial Research, India for financial assistance to one of the author Mr. Inamuddin.

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Electrochimica Acta 53 (2008) 5540–5548

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Preparation, physico-chemical characterization and electrical conductivity measurement studies of an organic–inorganic nanocomposite cation-exchanger: Poly-*o*-toluidine Zr(IV) phosphate

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ARTICLE INFO

Article history:
Received 6 December 2007
Received in revised form 28 February 2008
Accepted 1 March 2008
Available online 18 March 2008

Keywords:
Organic–inorganic composite material
Cation-exchanger
Electrical conductivity
Poly-*o*-toluidine Zr(IV) phosphate

ABSTRACT

An organic–inorganic nanocomposite cation-exchanger, i.e. poly-*o*-toluidine Zr(IV) phosphate was synthesized via sol–gel mixing of an electrical conducting polymer poly-*o*-toluidine into the matrices of inorganic precipitate of Zr(IV) phosphate. The ion-exchange capacity, chemical stability, effect of eluant concentration, elution behavior, pH titration and thermal studies were also carried out to understand the ion-exchange capabilities. The physico-chemical properties of the material were determined using AAS, CHN elemental analysis, FTIR, TGA–DTA, XRD, TEM and SEM studies. On the basis of distribution studies, the material was found to be highly selective for Hg(II). Its selectivity was examined by achieving some important binary separations like Hg(II)–Pb(II), Hg(II)–Cu(II), Hg(II)–Co(II), Hg(II)–Fe(III), Hg(II)–Sr(II), etc. on its column. This material possessed d.c. electrical conductivity in the semi-conducting range, i.e. 10^{-3} to 10^{-2} S cm^{-1}; measured by four-in-line probe d.c. electrical conductivity-measuring technique. The d.c. electrical conductivity of the composite material was found stable upto 110 °C for the composites under ambient conditions.

1. Introduction

Electrical conducting organic–inorganic composites are advanced class of materials [1] used as cationic exchanger [2–4] with various possible application such as in making ion-selective membrane electrode, separations of heavy metals from waste water. Organic polymeric part of the composite provide mechanical and chemical stability, where as inorganic part support the ion-exchange behavior, thermal stability and also increase the electrical conductivity. Such a modified composite materials can be applied as electrochemically switchable ion-exchanger [5,6] for water treatment, especially water softening. This ion-exchanger can be regenerated without chemical additives or water electrolysis. The conducting polymer-based nanocomposites have shown great potential in gas sensing [7]. One type of the composites contains a conducting polymer (polypyrrole, polyaniline, etc.) and metal oxides of iron [8,9]. Nanocomposite [10,11] contains polymer (poly-*o*-toluidine) and inorganic ion-exchange material (thorium(IV) phosphate) prepared by sol–gel method has shown conducting behavior and excellent ion-exchange properties with electrochemical application.

The following study summarizes the preparation, characterization and electrical conducting behavior of nanocomposite poly-*o*-toluidine Zr(IV) phosphate. Separation of metal ions have been performed on the surface of the material. The material is found more thermally stable than other materials of this class.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, GSC, E-merck (India). All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India), a double beam atomic absorption spectrophotometer (GBC 902, Australia), a digital flame photometer (Elico CL 22D, India), a UV/vis spectrophotometer (Elico El 301E, India), a water bath incubator shaker, a four-in-line probe d.c. electrical conductivity-measuring instrument (Scientific Equipment, India) were used.

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doi:10.1016/j.electacta.2008.03.002

2.2. Preparation of reagent solutions

0.1 M solutions of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and phosphoric acid (H_3PO_4) of different molarities were prepared in 4 M HCl and demineralised water (DMW), respectively. Solutions of 20% (v/v) o-toluidine (C_7H_9N) and 0.4 M ammonium persulphate ($(NH_4)_2S_2O_8$) were prepared in 2 M HCl.

2.3. Synthesis of polymer

2.3.1. Synthesis of poly-o-toluidine

The organic polymer derivative of polyaniline that is poly-o-toluidine was prepared by mixing in similar volume ratios of the solution of 0.4 M ammonium persulphate prepared in 4 M HCl into 20% o-toluidine prepared in 2 M HCl with continuous stirring by a magnetic stirrer for 2 h at 0 °C; a green-colored gel was obtained. The gel was kept for 24 h at 0 °C.

2.4. Synthesis of inorganic precipitate

2.4.1. Synthesis of zirconium(IV) phosphate

The method of preparation of the inorganic precipitate of Zr(IV) phosphate ion-exchanger was very similar to that of Alberti and Constantino [12], with slight modification [13] by mixing a solution of 0.1 M $ZrOCl_2 \cdot 8H_2O$ in 4 M HCl at the flow rate at 0.5 ml min^{-1} to an aqueous solution of H_3PO_4 in different molarities. The pH of the solution was maintained at 2 and constant stirring was done during mixing using a magnetic stirrer at room temperature (25 + 2 °C). The white-colored gel was left for 24h at room temperature for digestion.

2.5. Preparation of poly-o-toluidine Zr(IV) phosphate composite cation-exchange material

The composite cation-exchanger was prepared by the sol–gel mixing of poly-o-toluidine, an organic polymer, into the inorganic precipitate of zirconium(IV) phosphate. In this process, when the gels of poly-o-toluidine were added to the white inorganic precipitate of zirconium(IV) phosphate with a constant stirring, the resultant mixture were turned slowly into a greenish black-colored slurries. The resultant greenish black-colored slurries were kept for 24 h at room temperature.

Now the poly-o-toluidine-based composite gels were filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of ammonium persulphate. The washed gel was dried over P_2O_5 at 40 °C in an oven. The dried product was washed again with acetone to remove oligomers present in the material, and dried at 40 °C in an oven. The dried product was cracked into small granules and converted into H^+-form by treating with 1 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid two to three times. The excess acid was removed after several washings with DMW and finally dried at 50 °C. The particle size of approximately 125 μm of the composite cation-exchanger was obtained by sieving and stored in desiccators. The composite cation-exchanger having maximum capacity (1.71 mequiv. dry g^{-1}) as compared to Zr(IV) phosphate (1.46 mequiv. dry g ^{1}), was selected for the detailed studies of ion-selective electrode preparation. The condition of preparation and the ion-exchange capacity (IEC), physical appearance of the composite cation-exchanger poly-o-toluidine Zr(IV) phosphate (sample S-5) are given in Table 1.

Table 2
Ion-exchange capacity of various exchanging ions on poly-o-toluidine Zr(IV) phosphate composite cation-exchanger

Exchanging ions	pH of the metal solutions	Ionic radii (Å)	Hydrated ionic radii (Å)	Ion-exchange capacity (mequiv. dry g^{-1})
Li^+	3.3	0.68	3.40	0.95
Na^+	4.99	0.97	2.76	1.71
K^+	6.5	1.33	2.32	2.07
Mg^{2+}	4.87	0.78	7.00	1.08
Ca^{2+}	6.2	1.06	6.30	1.64
Sr^{2+}	6.3	1.27	-	2.18
Ba^{2+}	6.5	1.43	5.90	1.36

2.6. Ion-exchange properties of poly-o-toluidine Zr(IV) phosphate

2.6.1. Ion-exchange capacity

Poly-o-toluidine Zr(IV) phosphate is a cation-exchanger. The exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation-exchanger was determined by standard column process. One gram (1 g) of the dry cation-exchanger, sample S-5 in the H^+-form was taken into a glass column having an internal diameter (i.d.) ~1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5-cm long. 1 M alkali and alkaline earth metal nitrates as eluants were used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard (0.1 M) NaOH solution for the total ions liberated in the solution using phenolphthalein indicator and the IEC in mequiv. g^{-1} are given in Table 2.

2.6.2. Effect of eluant concentration

To find out the optimum concentration of the eluant for complete elution of H^+ ions, a fixed volume (250 ml) of sodium nitrate ($NaNO_3$) solution of varying concentrations were passed through a column containing 1 g of the exchanger in the H^+-form with a flow rate of ~0.5 ml min^{-1}. The effluent was titrated against a standard

Table 1
Conditions of preparation and the ion-exchange capacity of poly-o-toluidine Zr(IV) phosphate composite cation-exchange material

Sample	Mixing volume ratio					Appearance of beads after dying	Na^+ ion-exchange capacity (mequiv. dry g^{-1})
	0.1 M $ZrOCl_2 \cdot 8H_2O$ in 4 M HCl	H_3PO_4 in DMW	pH of the inorganic precipitate	0.4 M $(NH_4)_2S_2O_8$ in 2 M HCl	20% o-toluidine in 2 M HCl		
S-1	1	1 (2 M)	1	-	-	White granular	0.34
S-2	1	1 (2 M)	2	-	-	White granular	1.46
S-3	-	-	-	1	1	Greenish granular	0.7
S-4	1	1 (2 M)	2	1	1	Greenish black	0.77
S-5	1	2 (3 M)	2	1	1	Greenish black	1.71
S-6	1	1.5 (3 M)	2	1	1	Greenish black	0.95
S-7	0.5	1 (2 M)	2	1	1	Greenish black	0.35
S-8	1	2.5 (3 M)	2	1	1	Greenish black	1.31
S-9	1	1.5 (2 M)	2	1	1	Greenish black	0.54
S-10	1	1.5 (1 M)	2	1	1	Greenish black	0.9

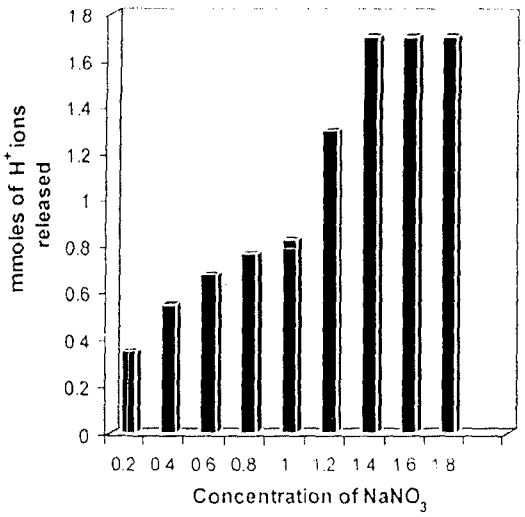


Fig. 1. Concentration plot of poly-o-toluidine Zr(IV) phosphate.

alkali solution of 0.1 M NaOH for the H^+ ions eluted out. A maximum elution was observed with the concentration of 1.4 M $NaNO_3$ as indicated in Fig. 1.

2.6.3. Elution behavior

Since with optimum concentration for a complete elution was observed to be 1.4 M for sample S-5, a column containing 1 g of the exchanger in H^+-form was eluted with $NaNO_3$ solution of this concentration in different 10 ml fractions with minimum flow rate as described above and each fractions of 10 ml effluent was titrated against a standard alkali solution for the H^+ ions eluted out. This experiment was conducted to find out the minimum volume necessary for almost complete elution of H^+ ions, which determines the exchange efficiency of the column as shown in Fig. 2.

2.6.4. pH-titration

pH-titration studies of poly-o-toluidine Zr(IV) phosphate (S-5) was performed by the method of Topp and Pepper [14]. A total of 500 mg portions of the cation-exchanger in the H^+-form were placed in each of the several 250 ml conical flasks, followed by the addition of equimolar solutions of alkali metal chlorides and

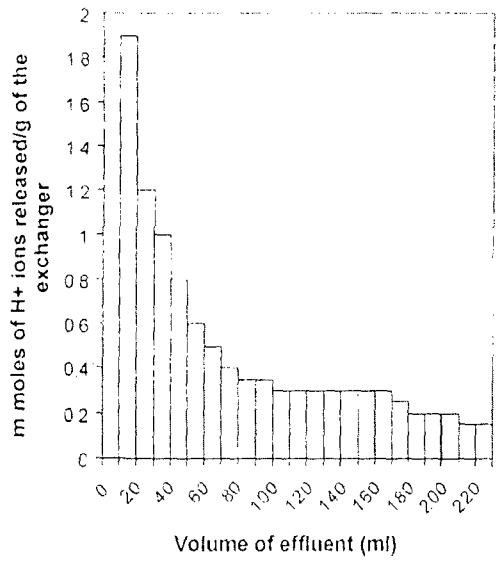


Fig. 2. Histogram showing the elution behavior of poly-o-toluidine Zr(IV) phosphate cation-exchange material.

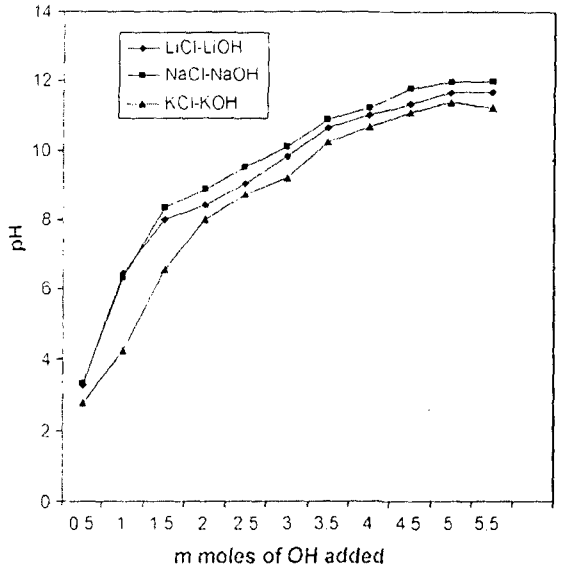


Fig. 3. pH-titration curves for poly-o-toluidine Zr(IV) phosphate composite cation-exchanger with various alkali metal hydroxides.

their hydroxides in different volume ratios, the final volume was kept 50 ml to maintain the ionic strength constant. The pH of the solution was recorded every 24 h until equilibrium was attained which needed ~5 days and pH at equilibrium was plotted against the milliequivalents of OH^- ions added (Fig. 3).

2.7. Physico-chemical properties of poly-o-toluidine Zr(IV) phosphate composite cation-exchange material

2.7.1. Chemical dissolution

250 mg portions of the composite cation-exchanger (poly-o-toluidine Zr(IV) phosphate, S-5) in H^+-form were treated with 20 ml each of different acids, bases, salt, organic solvents and also with DMW for 24 h with occasional shaking. The supernatant liquids were analyzed for 'zirconium' by ICP-MS while phosphate was determined as usual by the phosphovanado molybdate method [15].

2.7.2. Chemical composition

To determine the chemical composition of poly-o-toluidine Zr(IV) phosphate (sample S-5), 200 mg of the sample was dissolved in 20 ml of concentrated H_2SO_4. The material was analyzed for 'zirconium(IV)' by ICP-MS and phosphate by the phosphovanado molybdate method. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis. The weight percent composition of the material is presented in Table 3.

2.7.3. Thermal effect on IEC

To study the effect of drying temperature on the IEC, 1 g samples of the composite cation-exchange material (S-5) in the H^+-form

Table 3
Percent composition of poly-o-toluidine Zr(IV) phosphate (S-5) composite cation-exchanger

Serial no.	Element	Percentage
1	Zr	26.3
2	P	12.5
3	C	38.8
4	H	4.5
5	N	7.9
6	O	10.0

Table 4
Thermal stability of poly-o-toluidine Zr(IV) phosphate (S-5) after heating to various temperatures for 1 h

Heating temperature (°C)	Appearance (color)	Weight loss (%)	Na^+ ion-exchange capacity (mequiv. dry g^{-1})	% retention of IEC
50	Black	-	1.71	100
100	Black	4.00	1.71	100
150	Black	8.00	1.71	100
200	Black	16.00	0.864	50.53
300	Black	27.20	0.834	48.77
400	Black	35.20	0.762	44.56
450	Light gray	47.40	0.864	50.53
500	Light gray	63.60	0.885	51.75
600	Light gray	68.20	0.372	21.75
650	Light gray	68.08	0.348	20.94
700	Light gray	69.40	0.317	18.54

were heated at various temperatures in a muffle furnace for 1 h and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature. The results are given in Table 4.

Simultaneous TGA–DTA studies were also carried out on heating the sample S-5 (as prepared) upto 1000 °C at a constant rate (10 °C min^{-1}) in the air atmosphere.

2.8. Thermal (TGA and DTA) studies

Simultaneous TGA and DTA studies of the composite cation-exchange material (poly-o-toluidine Zr(IV) phosphate, S-5) in original form were carried out by an automatic thermobalance on heating the material from 10 to 900 °C at a constant rate (10 °C min^{-1}) in the air atmosphere (air flow rate of 200 ml min^{-1}) as shown in Fig. 4.

2.9. FTIR (Fourier transform infrared) studies

The FTIR spectrum of poly-o-toluidine (sample S-3); Zr(IV) phosphate (sample S-2) and poly-o-toluidine Zr(IV) phosphate (sample S-5) in the original form dried at 50 °C were taken by KBr disc method at room temperature and is given in Fig. 5.

2.10. X-ray analysis

Powder X-ray diffraction (XRD) patterns were obtained in an aluminium sample holder for the sample S-5 (poly-o-toluidine Zr(IV) phosphate) in the original form using a PW 1148/89-based diffractometer with Cu Kα radiations and is shown in Fig. 6.

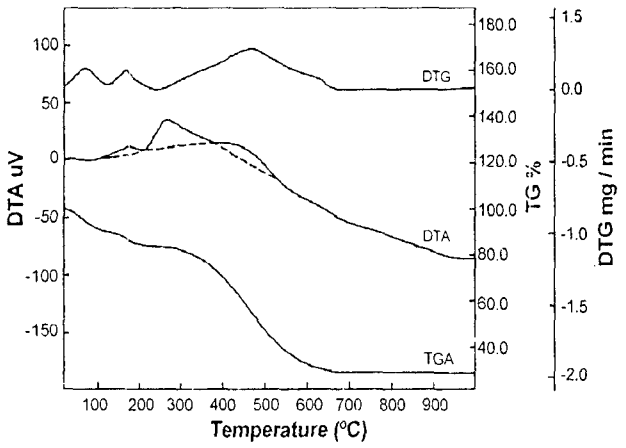


Fig. 4. Simultaneous TGA–DTA curves of poly-o-toluidine Zr(IV) phosphate (as prepared).

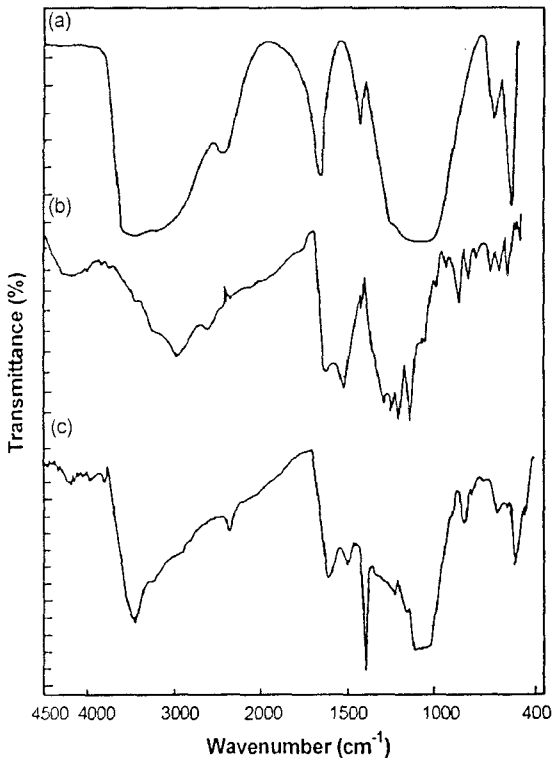


Fig. 5. FTIR spectra of as prepared poly-o-toluidine (a), Zr(IV) phosphate (b) and poly-o-toluidine Zr(IV) phosphate composite material (c).

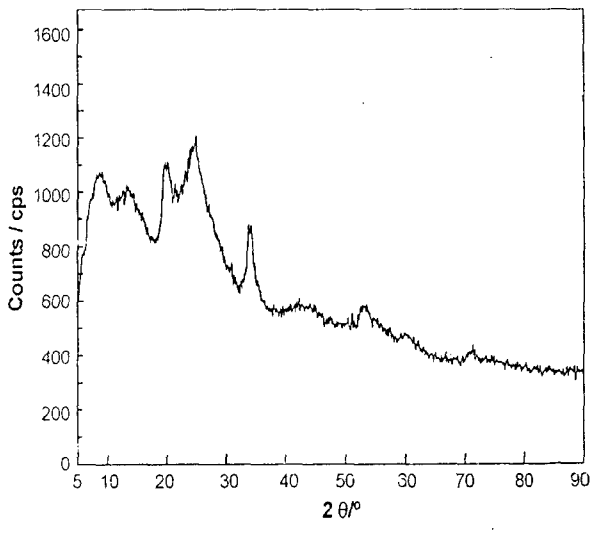


Fig. 6. Powder X-ray diffraction pattern of poly-o-toluidine Zr(IV) phosphate (as prepared).

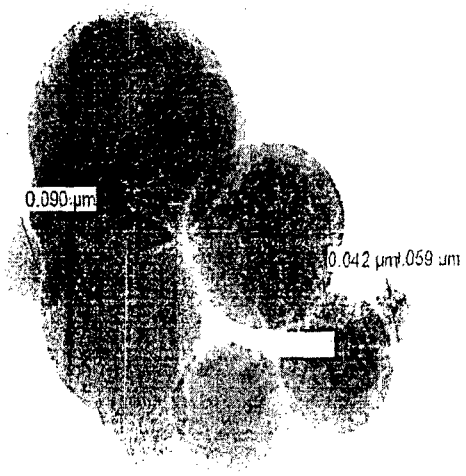


Fig. 7. Transmission electron microscopy (TEM) shows the particle size of poly-o-toluidine Zr(IV) phosphate cation-exchange material.

2.11. TEM (transmission electron microscopy) studies

TEM studies were carried out to know the particle size of the poly-o-toluidine Zr(IV) phosphate composite cation-exchange material as shown in Fig. 7.

2.12. SEM (scanning electron microscopy) studies

Microphotographs of the original form of poly-o-toluidine, (S-3); inorganic precipitate of Zr(IV) phosphate, (S-2); organic–inorganic composite materials poly-o-toluidine zirconium(IV) phosphate, (S-5) were obtained by the scanning electron microscope at various magnifications as shown inFig. 8.

2.13. Selectivity (sorption) studies

The distribution behavior of metal ions plays an important role in the determination of selectivity of the material. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution coefficients of the counter ions.

The distribution coefficient (K_d values) of various metal ions on poly-o-toluidine Zr(IV) phosphate were determined by batch method in various solvents systems. Various 200 mg of the composite cation-exchanger beads (S-5) in the H^+-form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium and kept for 24 h with continuous shaking for 6 h in a temperature-controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The initial metal ion concentration was to adjust that it did not exceed 3% of its total ion-exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005 M solution of EDTA [16]. Some heavy metal ions such as [Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}] were determined by atomic absorption spectropho-

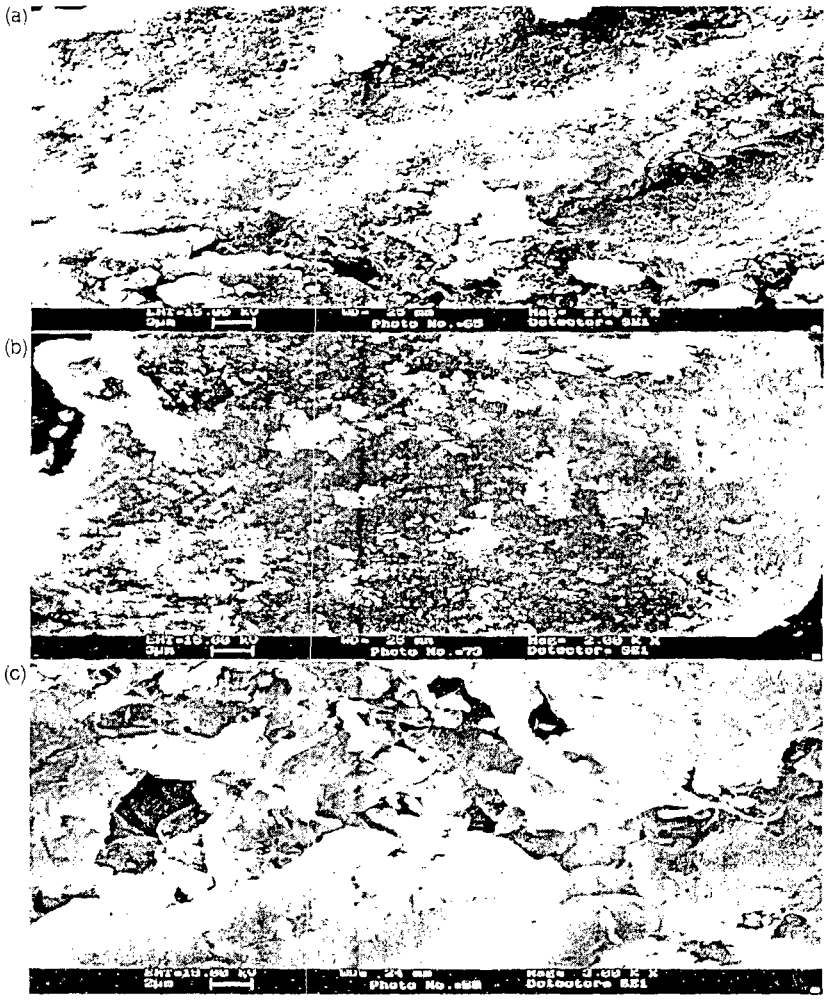


Fig. 8. Scanning electron microphotographs (SEM) of chemically prepared (a) poly-o-toluidine at the magnification of 3500×, (b) Zr(IV) phosphate at the magnification of 3000× and (c) poly-o-toluidine Zr(IV) phosphate composite system at the magnification of 2500×.

tometry (AAS). The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase. In other word, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion-exchange material and hence mathematically can be calculated using the formula given as:

$$K_d\,(\mathrm{ml\,g^{-1}}) = \frac{m \text{ moles of metal ions / g of ion-exchanger}}{m \text{ moles of metal ions / ml of solution}} \quad (1)$$

$$\text{i.e. } K_d\,(\mathrm{ml\,g^{-1}}) = \frac{(I-F)}{F}\frac{V}{M} \quad (2)$$

where I is the initial amount of metal ion in the aqueous phase, F is the final amount of metal ion in the aqueous phase, V is the volume of the solution (ml) and M is the amount of cation-exchanger (g).

2.14. Quantitative separation of metals ions

Quantitative binary separations of some important metal ions of analytical utility were achieved on poly-o-toluidine Zr(IV) phosphate column. 1 g of the cation-exchanger, S-5 (~125 μm) in H^+-form were used for column separations in a glass tube having an internal diameter of ~0.6 cm and a height of 35 cm. The column was washed thoroughly with DMW and the mixture of two metal ions having initial concentrations of 0.01 M each, to be separated was loaded on it and allowed for 1 h to absorb the metal ions on the exchanger and pass on to the column gently (maintaining a flow rate of 2–3 drops per min) till the level was above the surface of the material. After recycling two or three times to ensure complete absorption of the mixture on column beads, the separation was achieved by passing a suitable solvent at a flow rate of 1 ml min^{-1} through the column as eluent. The metal ions in the effluent were determined quantitatively by AAS and EDTA titration.

2.15. Electrical conductivity measurements

2.16. Sample (pellet) preparation

The sample material was dried completely at 45 and 50 °C in an oven. Then 200 mg material was finely grounded in a mortar pastel and pellets were made at room temperature with the help of hydraulic pressure instrument at 25 kN pressure for 20 min. The thickness of pellets was measured by a micrometer at five different points and the average thickness was taken as the thickness of the pellet sample. Electrical conductivity studies were performed on pressed material.

The d.c. electrical conductivity of an electrically conducting composite cation-exchanger poly-o-toluidine Zr(IV) phosphate (S-5) as prepared and treated with 1 M HCl solution, was measured on pressed pallets of composite material with increasing temperature (30–180 °C) by using a four-in-line probe d.c. electrical conductivity-measuring instrument.

After the measurements of current–voltage data from the instrument, the electrical conductivity of the solid samples can be calculated using the following equation:

$$\sigma = \frac{\sigma_0}{G_7(W/S)} \quad (3)$$

where σ is the electrical conductivity in S/cm, G_7 (W/S) is the correction factor used for the case of non-conducting bottom surface and it is a function of W, thickness of the sample under test (cm) and S, probe spacing (cm), i.e.

$$G_7\left(\frac{W}{S}\right) = \left(\frac{2S}{W}\right)\log_e 2 \quad (4)$$

and

$$\sigma_0 = I(V2\pi S) \quad (5)$$

where I is the current (A) and V is the voltage (V).

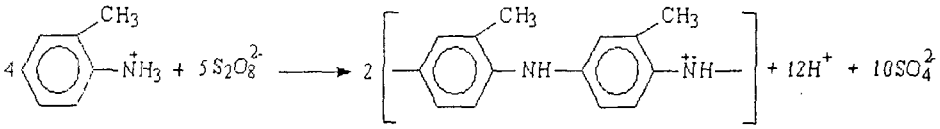
This composite material was also treated with 1 M NaCl, KCl, $ZnCl_2$, $Pb(NO_3)_2$, $MgCl_2$ and $Cu(NO_3)_2$ solutions, and electrical conductivity measurements were carried out on these different forms (Na^+, K^+, Zn^{2+}, Pb^{2+}, Mg^{2+} and Cu^{2+}), of composite cation-exchange materials.

The isothermal stability of poly-o-toluidine Zr(IV) phosphate composite in terms of d.c. electrical conductivity retention was carried out on the selected samples (treated with 1 M HCl) at 50, 70, 90, 110 and 130 °C in an air oven.

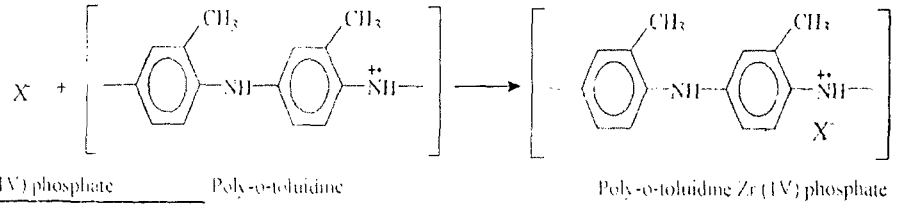
3. Results and discussion

The main objective of this research work is to add a new material in advance class of electrically conducting nanocomposite cation-exchange materials. Thus various samples of organic–inorganic electrically conducting nanocomposite poly-o-toluidine Zr(IV) phosphate were chemically prepared by sol–gel mixing of organic polymer poly-o-toluidine into inorganic precipitate Zr(IV) phosphate (Table 1). Among them sample S-5 was selected due to its better Na^+ ion-exchange capacity (1.71 mequiv. dry g^{-1}) as compared to Zr(IV) phosphate (1. 46 mequiv. dry g^{-1}), high percentage of yields, chemical, mechanical and thermal stabilities.

Poly-o-toluidine gel was prepared by oxidation coupling using $(NH_4)_2S_2O_8$ in acidic medium [17] as given in the following reaction:



The binding of poly-o-toluidine into the matrix of Zr(IV) phosphate is possible due to ionic interactions between the radical cation of poly-o-toluidine and anionic groups of Zr(IV) phosphate as given in the following reaction:



The ion-exchange capacity of the composite cation-exchanger for alkali metal ions and alkaline earth metal ions increased according to the decrease in their hydrated ionic radii shown in Table 2. The

Table 5
K_d values of some metal ions on poly-o-toluidine Zr(IV) phosphate column in d fferent solvent systems

Metal ions	Pb^{2+}	Hg^{2+}	Cu^{2+}	Co^{2+}	Cd^{2+}	Zn^{2+}	Ni^{2+}	Mn^{2+}	Fe^{3+}	Al^{3+}	Ba^{2+}	Zr^{4+}	Th^{2+}	Sr^{2+}
DMW	116	476	200	67	157	1900	60	150	233	44	150	125	150	83
0.1 M HCl	40	-	11	5	54	23	25	-	275	200	37	100	33	20
0.01 M HCl	55	-	16	25	60	45	77	100	66	60	50	100	750	46
0.1 M HNO_3	40	715	12	16	30	31	133	100	300	400	40	600	166	6
0.01 M HNO_3	50	433	75	66	60	23	175	350	42	45	380	100	233	30
10% formic acid	38	-	13	24	-	-	60	-	150	66	-	75	-	-
20% formic acid	81	130	-	59	-	-	30	-	166	233	-	66	-	-
30% formic acid	114	-	6	59	-	-	55	-	200	133	-	33	-	-
10% ethanol	114	585	233	100	200	100	200	200	225	23	550	100	100	54
20% ethanol	54	520	166	66	172	114	60	200	66	60	175	66	150	100
10% acetone	116	1560	233	47	133	100	50	22	125	114	333	80	300	100
pH 3.75	200	357	233	66	325	172	150	-	100	40	366	40	50	157
pH 5.75	16	1820	45	63	233	100	60	150	400	150	242	100	75	171
0.1 M H_2SO_4	40	1083	17	108	23	7	66	-	250	-	220	100	150	220
0.01 M H_2SO_4	133	520	37	81	36	23	55	44	100	66	100	75	-	100

minimum molar concentration of $NaNO_3$ as eluant for sample S-5 was 1.4 M for maximum release of H^+ ions from 1 g of the cation-exchanger as evident from Fig. 1. The elution behavior indicated that the exchange is quite fast because only 250 ml of sodium nitrate solution (1.4 M) is enough to release the total H^+ from 1 g of poly-o-toluidine Zr(IV) phosphate cation-exchange material (Fig. 2).

The pH-titration curves for poly-o-toluidine Zr(IV) phosphate (sample S-5) was obtained under equilibrium conditions with NaOH/NaCl, KOH/KCl and LiOH/LiCl, systems indicating bifunctional behavior of the materials as shown in Fig. 3. The rate of H^+–K^+ exchange was faster than those of H^+–Na^+ and H^+–Li^+ exchanges.

The percent composition of Zr, P, C, H, N and O in the material was found to be 26.3, 12.5, 38.75, 4.478, 7.938 and 10.034. The molar ratio of Zr, P, C, H, N and O in the material estimated as 1:1.3:11:15:2:2.2, which suggest a tentative formula as $(ZrO_2)(H_3PO_4)(CH_3C_6H_4NH_2)$.

On heating at different temperatures for 1 h, the mass and physical appearance of the dried sample material (S-5) were changed as the temperature increased as shown in Table 4. The weight loss starts from 100 °C but without change of its ion-exchange capacity upto 150 °C. The material was found thermally stable upto 400 °C as the sample maintained 65% of its initial mass and without change in its color and appearance and it retains 50% of ion-exchange capacity. It may be due to the loss of external water molecule and condensation of material. Above 400 °C color of the material starts to change with loss of mass which indicate the decomposition of materials. The results also support the TGA studies.

The thermogravimetric analyses (TGA–DTA) curve (Fig. 4) of the material showed continuous weight loss of mass (about 10%) up to 150 °C, which may be due to the removal of external water molecule [18]. Further weight loss of mass in between 149 and 350 °C may be due to the condensation of intramolecular hydroxyl group. A steep weight loss of mass observed in the temperature range 350–500 °C may be due to the conversion of phosphate group to pyrophosphate. Slight decomposition of organic part may be observed in the temperature range 500–650 °C. At 650 °C onwards, a smooth horizontal section represented the complete formation of the oxide form of the material. The DTA curve shows the reaction is exothermic during the change of phase of material, broad peaks at 280 and 480 °C can be observed.

The FT-IR spectra of poly-o-toluidine, Zr(IV) phosphate and poly-o-toluidine Zr(IV) phosphate are shown in Fig. 5. The FTIR spectrum of the composite cation-exchanger, sample S-5 (Fig. 5c) showed the presence of extra water molecule in addition to the –OH groups and metal oxides present internally in the material. In the spectrum a strong broad band around 3400 cm^{-1} is found which could be attributed to –OH stretching frequency. The peak at the around 1600 cm^{-1} may be due to the interstitial water present in the composite material [19]. An assembly of three peaks in the 500–800 cm^{-1} region showed the presence of ionic phosphate groups [20] as well as metal oxygen bonds present in the material. The additional band at around 1400 cm^{-1} can be ascribed to stretching vibration of C–N [21]. This indicates that the material contains considerable amount of poly-o-toluidine. These vibration frequencies are in close resemblance with the FTIR spectrums of poly-o-toluidine (Fig. 5a) and poly-o-toluidine Zr(IV) phosphate (Fig. 5c).

The X-ray powder diffraction pattern of this cation-exchanger (sample S-5, as-prepared) recorded on powdered sample exhibited no peak in the spectrum (Fig. 6) suggesting an amorphous nature of the composite material. From the TEM studies it is clear (Fig. 7) that the poly-o-toluidine Zr(IV) phosphate cation-exchange material shows particle size range of 42.0–100.0 nm, thus the material particle size shows the nano-range.

SEM photographs of poly-o-toluidine, Zr(IV) phosphate and poly-o-toluidine Zr(IV) phosphate obtained at different magnifications (Fig. 8) indicate the adhesion between two phases, i.e. inorganic ion-exchange material with organic polymer(poly-o-toluidine). The SEM pictures showed the difference in surface morphology of organic polymer, inorganic precipitate and composite material. It has been revealed that after binding of poly-o-toluidine with Zr(IV) phosphate, the morphology has been changed.

In order to find out the potentiality of this composite material (S-5) in the separation of metal ions, distribution studies for 23

Table 6
Some binary separation of metal ions achieved on poly-o-toluidine Zr(IV) phosphate column

Separation achieved	Amount loaded (μg)	Amount found (μg)	% error	Eluent used	Volume of eluent (ml)
Pb(II)	4144.0	4144.0	0.0	pH 5.75	60
Hg(II)	2005.9	1973.8	-1.63	0.01 M HNO_3	50
Cd(II)	2248.22	2322.7	+3.21	0.1 M H_2SO_4	50
Hg(II)	3008.9	3028.9	+0.66	0.01 M HNO_3	50
Fe(III)	1116.94	1103.3	-1.24	0.01 M HNO_3	50
Hg(II)	3510.3	3560.5	+1.43	0.01 M HNO_3	50
Co(II)	1178.66	1226.7	+3.92	0.1 M HCl	60
Hg(II)	3108.2	3087.3	-0.67	0.01 M HNO_3	50
Cu(II)	1270.9	1270.9	0.0	0.1 M HCl	50
Hg(II)	4011.8	3967.6	-1.25	0.01 M HNO_3	50
Sr(II)	1752.4	1787.61	+1.97	0.1 M HNO_3	50
Hg(II)	3108.4	3159.8	+1.65	0.01 M HNO_3	50

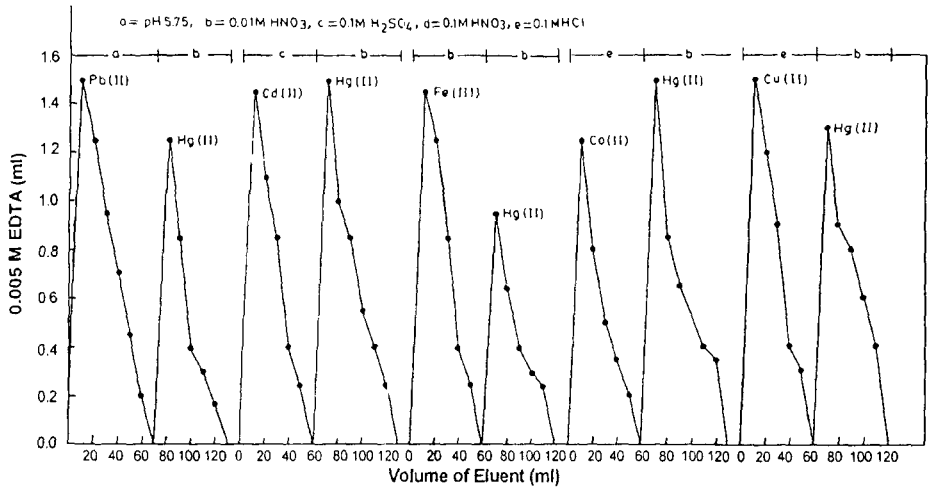


Fig. 9. Binary separations of Hg(II) from Pb(II), Cd(II), Fe(III), Co(II) and Cu(II) on poly-o-toluidine Zr(IV) phosphate column.

metal ions were performed in 10 solvent systems. The distribution studies (Table 5) showed that K_d values varied with the nature and composition of contacting solvents. It was also observed from the sorption studies (K_d values) that the composite has a maximum selectivity towards Hg^{2+} because mercury was highly adsorbed in all solvents, while remaining metal ions were poorly adsorbed.

The separation capacity of the material has been demonstrated by achieving some important binary separations, viz. Hg(II)-Cu(II), Hg(II)-Co(II), Hg(II)-Pb(II), Hg(II)-Fe(III), Hg(II)-Sr(II), etc. Table 6 summarizes the salient features of these separations. The order of elution and eluant used separation are given in Fig. 9. The separations are quite sharp and recovery is quantitative and reproducible.

Electrical conductivities of the pellets of poly-o-toluidine-based Zr(IV) phosphate composite samples were determined from the measurement of conductivity of the samples using the four-probe method of conductivity measurement for semiconductors. The variations of electrical conductivity (σ) of the poly-o-toluidine Zr(IV) phosphate composite samples (as prepared and HCl treated) (prepared with 20% o-toluidine concentration, vol.%) by raising temperatures (between 30 and 180 °C) are carried out. On examination, it was observed that the electrical conductivity of the sample increase with the increase in temperature and the values lie in the order of 10^{-3} to 10^{-2} S cm^{-1}, i.e. in the semiconductor region. Although the presence of organic groups (CH_3^-) in poly-o-toluidine should decrease the electrical conductivity, if it is compared with polyaniline composites (10^{-5} to 10^{-3} S cm^{-1}) [4], however electrical conductivity of this material is not effected. It may be due to the presence of Zr(IV) phosphate which is a good ion-exchanger. To determine the nature of dependence of electrical conductivity on temperature, plots of log σ versus 1000/T (K) were drawn and they

Table 7
Four-probe d.c. electrical conductivity of different forms of poly-o-toluidine Zr(IV) phosphate composite system at ambient temperature (prepared with 20% o-toluidine monomers)

Sample no.	Poly-o-toluidine Zr(IV) phosphate composite	Conductivity (S cm^{-1})
1	As prepared	1.08×10^{-2}
2	HCl treated	1.37×10^{-3}
3	NaCl treated	1.83×10^{-2}
4	$ZnCl_2$ treated	1.72×10^{-2}
5	KCl treated	8.10×10^{-4}
6	$Pb(NO_3)_2$ treated	4.19×10^{-2}
7	$MgCl_2$ treated	1.21×10^{-2}
8	$Cu(NO_3)_2$ treated	1.66×10^{-3}

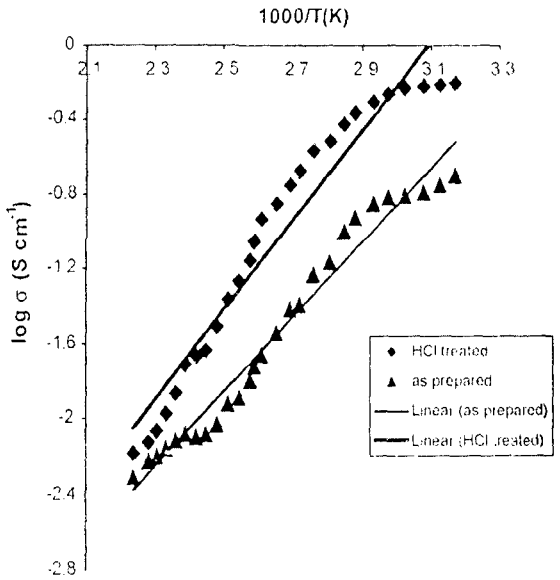


Fig. 10. Arrhenius plots for poly-o-toluidine Zr(IV) phosphate composite material.

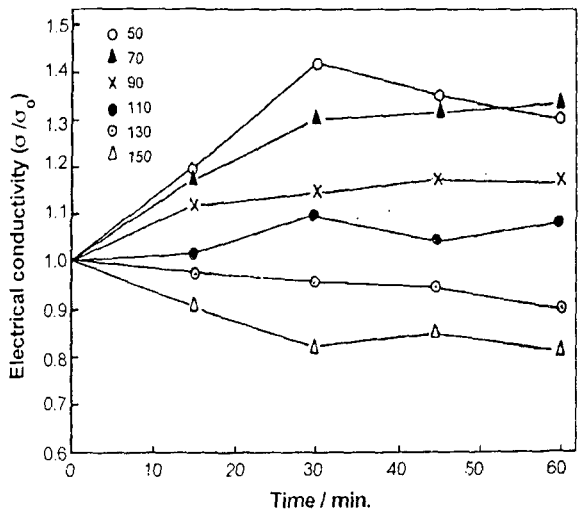


Fig. 11. Isothermal stability of poly-o-toluidine Zr(IV) phosphate composite (HCl treated) in terms of retention of d.c. electrical conductivity with respect to time at 50, 70, 90, 110, 130 and 150 °C.

followed Arrhenius equation similar to other semiconductors as shown in Fig. 10 [22]. It was also observed that the composite materials showed enhanced electrical conductivity on exposure to HCl as compared to original form, due to the charge-transfer reaction between poly-*o*-toluidine component of the composite and doping agent HCl. The energies of activation of electrical conduction for the composite samples (as prepared and HCl treated) calculated from the slopes of the Arrhenius plots were 19.97 and 16.58 eV, respectively.

This composite material was also treated with 1 M NaCl, $ZnCl_2$, $Pb(NO_3)_2$, KCl, $MgCl_2$ and $Cu(NO_3)_2$ solutions, and electrical conductivity measurements were carried out on these different forms (Na^+, Zn^{2+}, K^+, Pb^{2+}, Mg^{2+} and Cu^{2+}), of materials. It was observed that the sample treated with $Pb(NO_3)_2$ showed the higher electrical conductivity and treated with KCl and $Cu(NO_3)_2$ showed lower electrical conductivity at room temperature as given in Table 7.

The thermal stability of the composite material (HCl treated) in terms of d.c. electrical conductivity retention was studied under isothermal condition (at 50, 70, 90, 110, 130 and 150 °C) measuring four-probe-in-line d.c. electrical conductivity at an interval of 15 min. The electrical conductivity (σ/σ_0) versus time (min) is shown in Fig. 11. It was observed that the electrical conductivity for poly-*o*-toluidine Zr(IV) phosphate composite material is quite stable at 50, 70, 90 and 110 °C that supports the fact that the d.c. electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 and 150 °C that may be attributed to the loss of dopant and the chemical reaction of dopant with the material.

4. Conclusions

Poly-*o*-toluidine Zr(IV) phosphate, an organic–inorganic composite material synthesized by the sol–gel mixing have good ion-exchange capacity (1.71 mequiv. g^{-1}) as compared to Zr(IV) phosphate (1.46 mequiv. g^{-1}) providing a new material for advance class of nanocomposite cation-exchange material. TEM photograph shows the particle size of the composite material within the range of 42.0–100.0 nm and thus material can be considered as nanocomposite material. The characterization of poly-*o*-toluidine Zr(IV) phosphate is justified on the basis of FTIR, TGA–DTA, X-ray, SEM, elemental analysis and thermal treatment. It is also observed from the selectivity studies that the material is highly selective for Hg(II). The chromatographic potentiality of this composite cation-exchanger has been explored by achieving some important binary separations on its column. It is evident from the separation achieved that recoveries are quantitative and reproducible. It is quite clear from the fact that the composite cation-exchanger in a semiconductor lies in the range of 10^{-3} to 10^{-2} S cm^{-1}. It is also observed from isothermal technique of conductivity measurement that the material with respect to d.c. electrical conductivity is stable upto 110 °C.

Acknowledgements

The authors are thankful to Department of Applied Chemistry, Z.H. College of Engineering and Technology, A.M.U. (Aligarh) for providing research facilities. Assistance provided by the R.S.I.C. Bombay, I.I.T. Delhi and I.I.T. Roorkee to carry some instrumental analysis.

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Electrochimica Acta 54 (2009) 3320–3329

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Synthesis, characterization and ion-exchange properties of a fibrous type 'polymeric-inorganic' composite cation-exchanger Nylon-6,6 Sn(IV) phosphate: Its application in making Hg(II) selective membrane electrode

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ARTICLE INFO

Article history:
Received 8 September 2008
Received in revised form 2 December 2008
Accepted 18 December 2008
Available online 27 December 2008

Keywords:
Polymeric-inorganic composite material
Cation-exchanger
Nylon-6,6 Sn(IV) phosphate
Hg(II) ion-selective membrane electrode

ABSTRACT

A polymeric-inorganic composite cation-exchanger, i.e. Nylon-6,6 Sn(IV) phosphate was synthesized via mixing of polymer Nylon-6,6 into the matrices of inorganic precipitate of Sn(IV) phosphate to form composite cation-exchanger. Ion-exchange capacity (IEC), ion-exchange properties, thermal stability and distribution behavior, etc. were also carried out to understand the cation-exchange behavior of the material. The physico-chemical properties of the material were determined using AAS, CHN elemental analysis, FTIR, TGA-DTA, XRD, and SEM studies. On the basis of distribution studies, the material was found to be highly selective for Hg(II), a highly toxic environmental pollutant. Using this electroactive composite material, a new heterogeneous precipitate based selective membrane electrode was fabricated for the determination of Hg(II) ions in solutions. The membrane electrode is mechanically stable, with a quick response time, and can be operated within a wide pH range. The selectivity coefficients for different cations determined by mixed solution method were found to be less than unity. The electrode was also found to be satisfactory in potentiometric titrations.

1. Introduction

Synthetic organic–inorganic composite cation-exchange materials have received a great deal of attention because of their stability and reproducible analytical and electroanalytical applications [1–9]. Organic polymers of composite material provide the mechanical strength and increase the surface area for more available exchangeable sites of the inorganic part. Nano composites of organic–inorganic cation-exchange materials prepared by sol–gel method are advance class of materials that are expected to provide many possibilities [10,11]. Development of fibrous type organic–inorganic composite can also open more opportunities in their environmental application as they exhibit high efficiency in the process of sorption from liquid and gaseous media [12–18]. Paper like strips fabricated from such materials can be used as indicator in identification of various ions in polluted water. Such paper like strips may provide a new material in paper chromatographic techniques in separation and identification of different chemical species in a given sample.

Precipitate based ion-selective membrane electrodes are well known as they are successfully employed for determination of several anions and cations. The ion-selective membranes obtained by embedding ion-exchangers as electroactive materials in a polymer binder, i.e. epoxy resin (Araldite) or polystyrene or PVC, have been extensively studied as potentiometric sensors, i.e. ion sensors, chemical sensors or more commonly ion-selective electrodes.

In view of the above application of fibrous type material, Nylon-6,6 Sn(IV) phosphate composite material is developed in the present research work. The material is characterized and used in making Hg(II) ion-selective membrane electrode.

2. Experimental

2.1. Reagents and instruments

Reagents used for the synthesis of the material were obtained from CDH, GSC, E-merck (India). All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India), a double beam atomic absorption spectrophotometer (GBC 902, Australia), a digital flame photometer (Elico CL 22D, India), a UV/Vis spectrophotometer (Elico EI 301E, India), a water bath incubator shaker were used.

2.2. Preparation of reagent solutions

0.10 mol dm^{-3} Stannic chloride ($SnCl_4 \cdot 5H_2O$) solution was prepared in 4.0 mol dm^{-3} HCl, while 0.1 mol dm^{-3} disodium

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doi:10.1016/j.electacta.2008.12.038

Table 1
Conditions of preparation and the ion-exchange capacity of Nylon-6,6 Sn(IV)phosphate composite cation-exchange material.

Sample	Mixing volume ratio					Appearance of fiber after dying	Na^+ ion-exchange capacity in (m mol g^{-1})
	0.1 mol dm^{-3} $SnCl_4 \cdot 5H_2O$ in 4 mol dm^{-3} HCl	0.1 mol dm^{-3} Na_2HPO_4 in DMW	pH of the inorganic precipitate	Nylon-6,6 (gm)	Formic acid (ml)		
S-1	2	2	1	–	–	White granular	2.35
S-2	0.5	1.5	1	1	10	White fiber	1.47
S-3	1.5	1.5	1	2	10	White fiber	1.88
S-4	2	2	1	1	10	White fiber	2.1

hydrogen orthophosphate (Na_2HPO_4) solutions were prepared in demineralized water (DMW). Different amount of Nylon-6,6 were dissolved in different volume of concentrated formic acid.

2.3. Preparation of Nylon-6,6 Sn(IV) phosphate composite cation-exchange material

Stannic(IV) phosphate precipitates were obtained by adding 0.10 mol dm^{-3} stannic chloride ($SnCl_4 \cdot 5H_2O$) solution prepared in 4.0 mol dm^{-3} HCl at the flow rate of 0.50 cm^3 min^{-1} to solutions of 0.10 mol dm^{-3} disodium hydrogen orthophosphate (Na_2HPO_4) solution prepared in DMW of different molarities. The white precipitates were obtained, when the pH of the mixtures was adjusted 1.0 by adding aqueous ammonia with constant stirring. The gels of Nylon-6,6 prepared in concentrated formic acid were added into the white inorganic precipitate of Sn(IV) phosphate and mixed thoroughly with constant stirring. The white fibers were obtained which were kept for 24 h at room temperature for digestion. The supernatant liquid was decanted and fibers were filtered by suction. The excess acid was removed by several washings with DMW and the materials were dried in an air oven over P_4O_{10} at 40 °C. The dried products were converted to H^+-form by treating with 1.0 mol dm^{-3} HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and finally dried at 50 °C. Hence, a number of samples of 'Nylon-6,6 Sn(IV) phosphate' fibrous cation-exchanger were prepared (Table 1) and on the basis of Na^+ ion-exchange capacity (IEC), percentage of yield and physical appearance of material, sample S-4 was selected for detailed studies.

2.4. Ion-exchange properties of Nylon-6,6 Sn(IV) phosphate

2.4.1. Ion-exchange capacity (IEC)

1.0 g of the dry cation-exchanger, sample S-4 in the H^+-form was taken into a glass column having an internal diameter (i.d.) ~ 1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1.0 mol dm^{-3} alkali and alkaline earth metal nitrates as eluants were used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~0.5 cm^3 min^{-1}). The effluent was titrated against a standard (0.1 mol dm^{-3}) NaOH solution for the total ions liberated in the solution using phenolphthalein indicator and the IEC are given in Table 2.

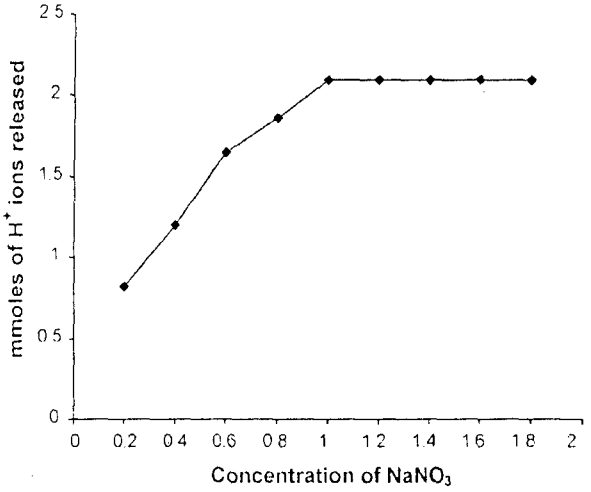

Fig. 1. Concentration plot of Nylon-6,6 Sn(IV) phosphate fibrous composite.

2.4.2. Effect of eluant concentration

To find out the optimum concentration of the eluant for complete elution of H^+ ions, a fixed volume (250 cm^3) of sodium nitrate ($NaNO_3$) solution of varying concentrations ranging from 0.20 to 1.60 mol dm^{-3} with a unit difference of 0.20 mol dm^{-3} were passed through a column containing 1 g of the exchanger in the H^+-form with a flow rate of ~0.5 cm^3 min^{-1}. The effluent was titrated against a standard alkali solution of 0.1 mol dm^{-3} NaOH for the H^+ ions eluted out. A maximum elution was observed with the concentration of 1.0 mol dm^{-3} $NaNO_3$ as indicated in Fig. 1.

2.4.3. Elution behavior

Since with optimum concentration for a complete elution was observed to be 1.0 mol dm^{-3} for sample S-4, a column containing 1 g of the exchanger in H^+-form was eluted with $NaNO_3$ solution of this concentration in different 10 cm^3 fractions with minimum flow rate as described above and each fractions of 10 cm^3 effluent was titrated against a standard alkali solution for the H^+ ions eluted

Table 2
Ion-exchange capacity of various exchanging ions on Nylon-6,6 Sn(IV) phosphate fibrous composite cation-exchanger.

Exchanging ions	pH of the metal solutions	Ionic radii (Å)	Hydrated ionic radii (Å)	Ion-exchange capacity (m mol g^{-1})
Li^+	6.70	0.68	3.40	0.95
Na^+	6.70	0.97	2.76	2.10
K^+	6.85	1.33	2.32	1.17
Mg^{2+}	6.50	0.78	7.00	1.98
Ca^{2+}	6.50	1.06	6.30	1.70
Sr^{2+}	6.30	1.27	–	1.50
Ba^{2+}	6.30	1.43	5.90	1.36

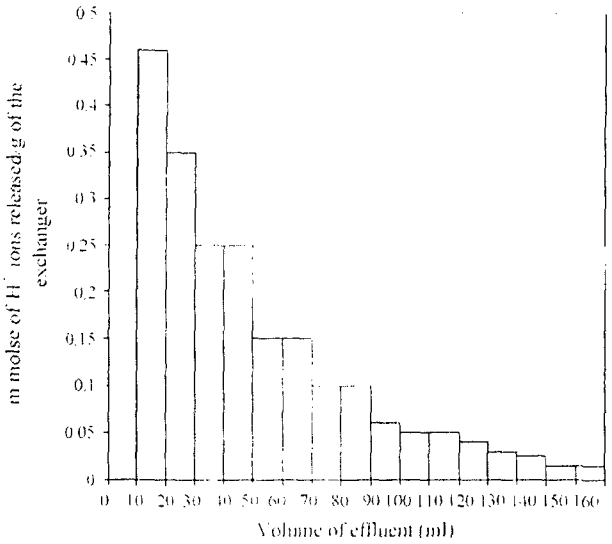

Fig. 2. Histogram showing the elution behavior of Nylon-6,6 Sn(IV) phosphate fibrous cation-exchange material.

out. This experiment was conducted to find out the minimum volume necessary for almost complete elution of H^+ ions, which determines the exchange efficiency of the column as shown in Fig. 2.

2.4.4. pH-titration

pH-titration studies of Nylon-6,6 Sn(IV) phosphate (S-4) was performed by the method of Topp and Pepper [19]. A total of 1.0 g portions of the cation-exchanger in the H^+-form were placed in each of the several 250 cm^3 conical flasks, followed by the addition of equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios, the final volume was kept 50 cm^3 to maintain the ionic strength constant. The pH of the solution was recorded every 24 h until equilibrium was attained which needed ~5 days and pH at equilibrium was plotted against the milliequivalents of OH^- ions added Fig. 3.

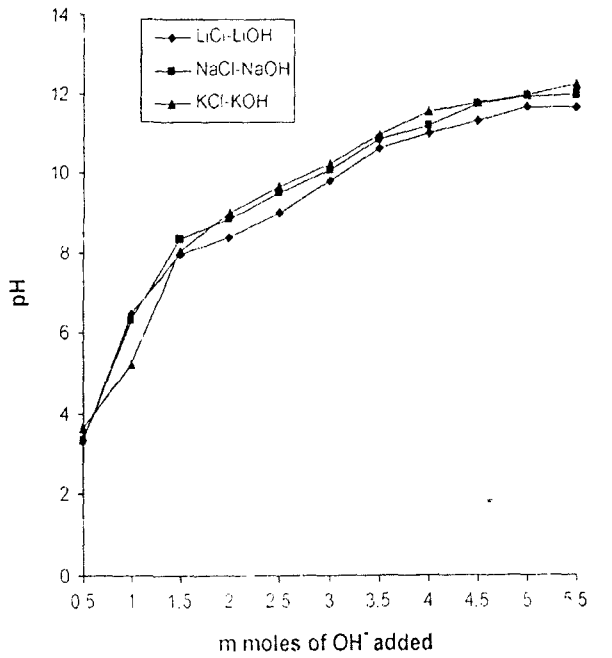

Fig. 3. pH-titration curves for Nylon-6,6 Sn(IV) phosphate fibrous composite cation exchanger with various alkali metal hydroxides.

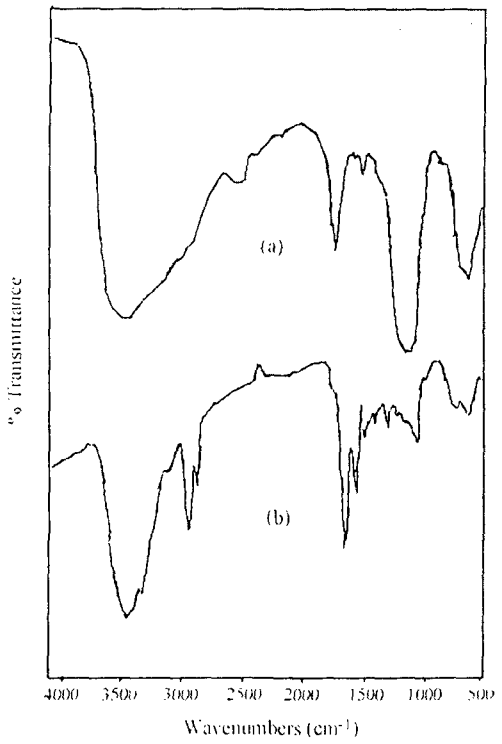

Fig. 4. FTIR spectra of as prepared Sn(IV) phosphate (a) and Nylon-6,6 Sn(IV)phosphate fibrous composite material (b).

2.5. Physico-chemical properties of Nylon-6,6 Sn(IV) phosphate composite cation exchange material

2.5.1. Chemical composition

To determine the chemical composition of Nylon-6,6 Sn(IV) phosphate (sample 4), 200 mg of the sample was dissolved in 20 cm^3 of concentrated H_2SO_4. The material was analyzed for 'tin(IV)' by ICP-MS and phosphate by the phosphovanado molybdate method [20]. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis.

2.5.2. Thermal effect on ion-exchange capacity (IEC)

To study the effect of temperature on the IEC, 1 g samples of the composite cation-exchange material (S-4) in the H^+-form were heated at various temperatures in a muffle furnace for 1 h and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature. The results are given in Table 3.

2.6. FTIR (Fourier Transform Infra Red) studies

The FTIR spectrum of Sn(IV) phosphate (sample S-1) and Nylon-6,6 Sn(IV) phosphate (sample S-4) in the original form dried at 50 °C were taken by KBr disc method at room temperature and is given in Fig. 4.

2.7. X-ray analysis

Powder X-ray diffraction (XRD) patterns were obtained in an aluminium sample holder for the sample S-4 (Nylon-6,6 Sn(IV) phosphate) in the original form using a PW 1148/89 based diffractometer with Cu Kα radiations and is shown in Fig. 5.

2.8. SEM (Scanning Electron Microscopy) studies

Microphotographs of the original form of inorganic precipitate of Sn(IV) phosphate (S-1), and fibrous composite materials Nylon-

Table 3
Thermal stability of Nylon-6,6 Sn(IV) phosphate (S-10) after heating to various temperatures for 1 h.

Heating temperature (°C)	Appearance (color)	Weight loss (%)	Na^+ ion-exchange capacity (m mol gm^{-1})	% Retention of IEC
50	White fiber	–	2.1	100
100	White fiber	–	2.1	100
150	Light brown	4.0	1.7	80.95
200	Light brown	6.5	1.46	69.52
250	Light brown	11.0	1.23	58.57
300	Light brown	18.7	0.95	45.24

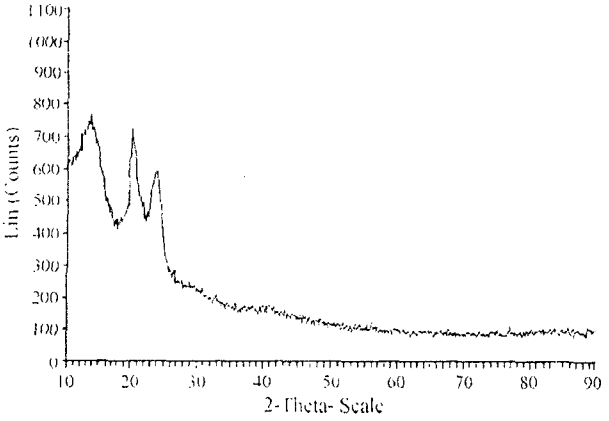

Fig. 5. Powder X-ray diffraction pattern of Nylon-6,6 Sn(IV) phosphate fibrous composite (as prepared).

6,6 Sn(IV) phosphate (S-4) were obtained by the scanning electron microscope at various magnifications as shown in Fig. 6.

2.9. Thermal (TGA and DTA) studies

Simultaneous TGA and DTA studies of the composite cation-exchange material (Nylon-6,6 Sn (IV) phosphate, S-4) in original form were carried out by an automatic thermobalance on heating the material from 50 to 900 °C at a constant rate (10 °C per min) in the air atmosphere (air flow rate of 200 ml min^{-1}) as shown in Fig. 7.

Fig. 6. Scanning electron microphotographs (SEM) of chemically prepared (a) Sn(IV) phosphate at the magnification of 3000× and (b) Nylon-6,6 Sn(IV) phosphate composite system at the magnification of 2500×.

2.10. Selectivity (sorption) studies

The distribution behavior of metal ions plays an important role in the determination of selectivity of the material. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution coefficients of the counter ions.

The distribution coefficient (K_d values) of various metal ions on Nylon-6,6 Sn(IV) phosphate were determined by batch method in various solvents systems. Various 0.20 g of the composite cation-exchanger material (S-4) in the H^+-form were taken in Erlenmeyer flasks with 20 cm^3 of different metal nitrate solutions in the required medium and kept for 24 h with continuous shaking for 6 h in a temperature controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The initial metal ion concentration was to adjust so that it did not exceed 3% of its total ion exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005 M solution of EDTA [21]. Some heavy metal ions such as [Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}] were determined by atomic absorption spectrophotometry (AAS). The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase. In other word, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion-exchange material and hence mathematically can be calculated using the formula given as:

$$K_d = \frac{m\,\text{moles of metal ions/gm of ion-exchanger}}{m\,\text{moles of metal ions/ml of solution}} (\text{ml g}^{-1}) \quad (1)$$

i.e.

$$K_d = (I - F)/F \times V/M (\text{ml g}^{-1}) \quad (2)$$

where I is the initial amount of metal ion in the aqueous phase, F is the final amount of metal ion in the aqueous phase, V is the volume of the solution (ml) and M is the amount of cation-exchanger (g).

3. Preparation of Nylon-6,6 Sn(IV) phosphate membrane electrode

The ion-exchange membrane was prepared by following the procedure of Coetzee and Benson [22]. Nylon-6,6 Sn(IV) phosphate cation-exchanger (100 mg) as electroactive material was ground to fine powder, and was mixed thoroughly with Araldite (Ciba-Geigy, India Ltd.) (100 mg) in 1:1 (w/w) ratio to make a homogeneous paste, which was then spread between the folds of Whatman's filter paper No. 42. Glass plates were kept below and above the filter paper folds as support. The phase of the exchanger and Araldite was kept under pressure of 2 kg cm^2 for 24 h and left to dry. Two sheets of different thickness 0.16, 0.20 mm of master membranes was prepared. These sheets were dipped in distilled water to remove filter paper. After drying, the membrane sheets were cut in the shapes of discs using a sharp edge blade.

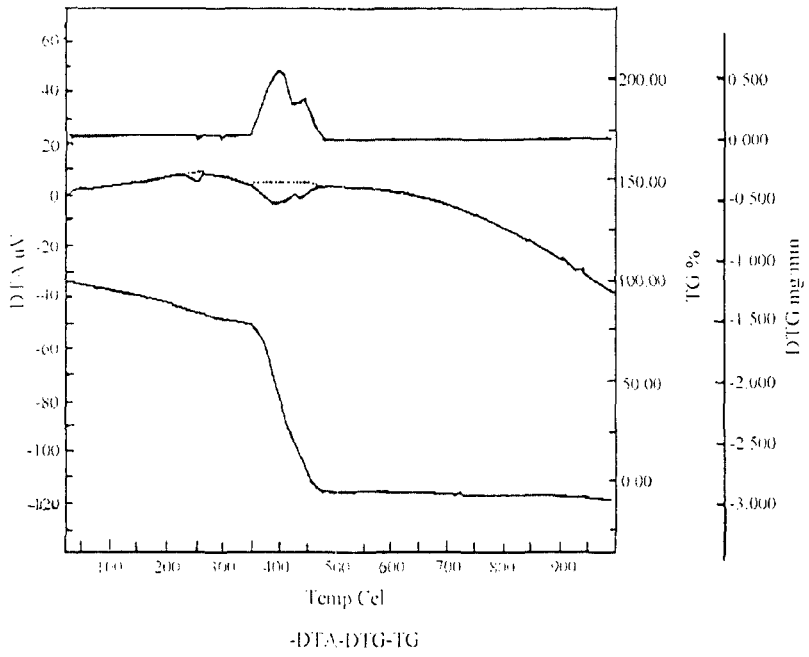

Fig. 7. Simultaneous TGA-DTA curves of Nylon-6,6 Sn(IV) phosphate fibrous composite (as prepared).

3.1. Characterization of membrane

The pre-requisite performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters were the membrane water content, porosity, thickness, swelling, etc. and were determined as described elsewhere [23–26] after conditioning the membrane, as given below.

3.2. Conditioning of the membrane

The membranes were conditioned by equilibrating with 1 M sodium chloride; about 1 ml of sodium acetate was also added to adjust the pH to 5–6.5 (to neutralize the acid present in the film).

3.3. Water content (% total wet weight)

The conditioned membranes were first soaked in water to elute any diffusible salts, blotted quickly with Whatman filter paper to remove surface moisture, and immediately weighed. These were further dried to a constant weight in a vacuum over P_4O_{10} for 24 h. The water content (% total wet weight) was calculated as:

$$\%\ \text{Total wet weight} = \frac{W_w - W_d}{W_w} \times 100, \quad (3)$$

where W_w is the weight of the soaked/wet membrane and W_d is the weight of the dry membrane.

3.4. Porosity

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data.

$$\varepsilon = \frac{W_w - W_d}{AL\rho_w} \quad (4)$$

where A is the area of the membrane, L is the thickness of the membrane and ρ_w is the density of water.

3.5. Thickness and swelling

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze.

Swelling was measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane. The results of the membrane characterization are given in Table 6.

3.6. Fabrication of ion-selective electrode

A membrane sheet (M-1) of 0.16 mm thickness, obtained by the above procedure, was cut in the shape of a disc and mounted at the lower end of a Pyrex glass tube (o.d. 1.6 cm, i.d. 0.8 cm) with Araldite. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with a 0.1 M mercuric nitrate $Hg(NO_3)_2$ solution. A saturated calomel electrode was inserted in the tube for electrical contact, and another saturated calomel electrode was used as an external reference electrode. The whole arrangement can be shown as follows:

Internal reference electrode (SCE)	Internal electrolyte 0.1 M Hg^{2+}	Membrane	Sample solution	External reference electrode (SCE)

3.7. Potential measurement and calibration

The performance of the response of the electrode in terms of the electrode potential (at 25 ± 2 °C), corresponding to the concentration of a series of standard solutions of $Hg(NO_3)_2$ (10^{-10}–10^{-1} M), prepared by serial dilution, was determined at a constant ionic strength, as described by IUPAC Commission for Analytical Nomenclature [27]. The membrane electrode was conditioned by soaking in a 0.1 M $Hg(NO_3)_2$ solution for 2 days and 1 h for at least before use. After performing, the experimental membrane electrode was removed from the test-solution and kept in a 0.1 M $Hg(NO_3)_2$ solution.

The data concerning the measured potential of the membrane electrode were plotted against selected concentrations of the

Table 4
K_d-values of some metal ions on Nylon-6,6 Sn(IV) phosphate column in different solvent systems.

Metal ions	Pb^{2+}	Hg^{2+}	Cu^{2+}	Co^{2+}	Cd^{2+}	Zn^{2+}	Ni^{2+}	Mg^{2+}	Fe^{3+}	Al^{3+}	Ba^{2+}	Sr^{2+}
DMW	62	50	25	67	43	41	60	150	60	25	33	83
10^{-1} mol dm^{-3} HNO_3	33	270	17	5	21	23	25	7	11	150	6	20
10^{-2} mol dm^{-3} HNO_3	20	40	15	25	7	45	7	–	14	20	–	46
10^{-3} mol dm^{-3} HNO_3	27	170	33	16	25	31	33	10	14	25	50	6
10^{-1} mol dm^{-3} HCl	114	200	8	66	29	23	75	6	10	200	9	30
10^{-2} mol dm^{-3} HCl	8	75	15	24	31	–	6	–	25	17	88	41
10^{-3} mol dm^{-3} HCl	33	30	25	59	50	33	30	–	100	11	233	25
10^{-1} mol dm^{-3} $HClO_4$	88	25	15	47	27	11	55	25	10	200	–	50
10^{-2} mol dm^{-3} $HClO_4$	22	78	33	15	36	21	20	6	11	30	41	24
10^{-3} mol dm^{-3} $HClO_4$	88	50	15	33	64	27	26	–	80	10	24	100
10^{-1} mol dm^{-3} H_2SO_4	100	23	27	25	15	10	50	22	–	50	100	17
10% Ethanol	50	150	31	9	50	14	15	14	200	200	67	14
10% Acetone	86	180	23	11	25	7	60	7	120	50	29	33

respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system. In order to study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time and working pH range.

3.8. Response time

The response time was measured by recording the e.m.f. of the electrode as a function of time when it was immersed in the solution to be studied. The electrode was usually first dipped in a 1×10^{-2} M solution of the ion concerned, and immediately shifted to another solution (~4.0) of 1×10^{-1} M ion concentration of the same ion (10 fold higher concentration). The potential of the solution was read at zero second, that is, just after immediate dipping of the electrode in the second solution, and subsequently recorded at intervals of 5 s. The potentials were then plotted against time. The time during which the potentials attained a constant value represents the response time of the electrode.

3.9. Effect of pH

A series of solutions of varying pH in the range of 1 to 14 were prepared, while keeping the concentration of the relevant ion constant (1×10^{-2} M). The pH variations were brought out by the addition of dilute acid (HCl) or dilute alkali (NaOH) solutions. The value of the electrode potential at each pH was recorded, and plotted against the pH.

3.10. Selectivity coefficients

To study the cationic interference due to other ions, the selectivity coefficients of various interfering cations for the ion-selective membrane electrode were determined by the mixed-solution method, as discussed elsewhere [28]. A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-2} M) and varying concentrations (1×10^{-1}–1×10^{-9} M) of the primary ion. The potential measurements were then made by using the membrane electrode assembly.

4. Preparation of PAN indicator strips

About 0.5 g fibrous composite material (Nylon-6,6 Sn(IV) phosphate) was dipped in PAN indicator for 24 h. The excess indicator was washed with DMW and the material was dried at 40 °C in an oven. The material was placed under hydraulic pressure machine at 25 KN pressure to obtain fibrous strip as shown in photograph of Fig. 13b. A drop of different concentration of some heavy metals such as Cu(II), Pb(II), Hg(II), Fe(II) was placed on strip. The color change was observed from the yellowish strip as shown in Table 5.

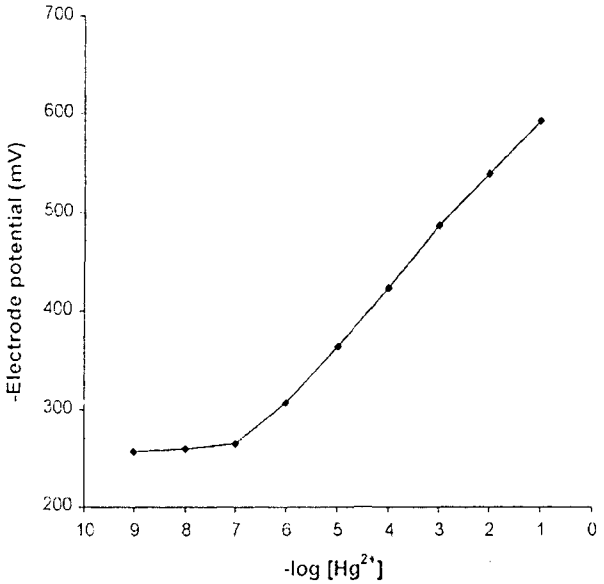

Fig. 8. Calibration curve for a Nylon-6,6 Sn(IV) phosphate membrane electrode in an aqueous solution of $Hg(NO_3)_2$.

Table 5
Change in color of fibrous PAN strip with different concentration of metal ions.

Concentration	Cu(II)	Pb(II)	Hg(II)	Fe(II)
200 ppm	Dark red	Dark red	Red	Red
100 ppm	Red	Red	Red	Red
50 ppm	Light red	Red orange	Orange	Yellow
10 ppm	Red orange	Orange	Orange	Yellow
5 ppm	Red orange	Yellow	Yellow	Yellow
2 ppm	Yellow	Yellow	Yellow	Yellow

5. Results and discussion

A fibrous composite Nylon-6,6 Sn(IV) phosphate was prepared by mixing inorganic precipitate of Sn(IV) phosphate and Nylon-6,6 developed in formic acid in different (w/v) ratio's as given in Table 1. The ion-exchange capacity of this composite material for alkali and alkaline earth metal ions was determined as shown in Table 2. It is noticed that ion-exchange capacity increases as hydrated radii decreases. The maximum ion-exchange capacity of the composite was found to be 2.1 meq/g for Na^+ ions.

The minimum molar concentration of $NaNO_3$ as eluant for sample S-4 was 1.0 mol dm^{-3} for maximum release of H^+ ions from 1 g of the cation-exchanger as evident from Fig. 1.

The efficiency of 1.0 g cation-exchanger column determined by the elution behavior indicate that the exchange is quite fast, as at the beginning all the exchangeable H^+ ions are eluted out in the first 150 cm^3 of the effluent (Fig. 2) within 5 h.

The pH-titration curve Fig. 3 showed sharp increase in pH when 1.0–2.0 m mol g^{-1} of NaOH, KOH and LiOH were added per gram of the cation-exchanger. Above this concentration the increase in pH is very slow. It may be due to the maximum release of H^+ from the exchanger site. Thus theoretical ion-exchange capacity of this material can be considered as 2.0 m mol g^{-1}.

The percent composition of Sn, P, C, H, N and O in the material was found to be 8.09, 0.95, 57.34, 9.76, 0.73, 23.13. A tentative structure can be proposed;

$$[Sn(HPO_4)_2\cdot(-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-)]\cdot nH_2O$$

Assuming that only the external water molecules are lost at 200 °C, the ~11 wt.% loss of mass represented by TGA curve must be due to the loss of nH_2O. Thus, from the above structure the value of 'n' the external water molecules can be calculated using Alberti's equation [29]:

$$18n = \frac{X(M + 18n)}{100}$$

where X is the percent weight loss (~11%) of the exchanger by heating upto 200 C and ($M + 18n$) is the molecular weight of the material. The calculations give 4.0 for the external water molecule (n) per molecule of the cation-exchanger (sample S-4).

Effect of heating at different temperature for 1 h, indicated that on heating at elevated temperature the mass, physical appearance and ion-exchange capacity of the dried fibrous cation-exchanger (S-4) was changed as the temperature increased as shown in Table 3. It was also observed that the hybrid cation-exchanger possessed higher thermal stability as the sample maintained about 80.0% of the initial mass by heating up to 150 C. However, in terms of ion-exchange capacity, this material was found stable up to 100 °C and it retained about 45.24% of the initial ion-exchange capacity by heating up to 300 °C.

Fig. 4 shows FTIR spectra of as-prepared Sn(IV) phosphate (a) fibrous composite (as prepared). The FTIR spectrum of cation-exchange material Nylon-6,6 Sn(IV) phosphate (Fig. 4b) revealed the presence of the external water molecules in addition to the metal–oxygen and metal–OH stretching band. In the spectrum a broad band in the region at 3434 cm^{-1} may be due to the presence of external water molecules. While a sharp peak in region 1638 cm^{-1} is referred to bending vibration of water. A less broad peak around in the region 1027 cm^{-1} may be due to the presence of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{2-}$ [30]. This fibrous cation-exchanger also showed a strong band at 1638 cm^{-1} corresponding to the carbonyl group of Nylon-6,6 and a small peak in the region 1465 cm^{-1} as a band of medium intensity mainly due to the C–H bending of methylene groups of nylon-6,6 moiety [31]. The absorption band in the region 1542 cm^{-1} may be due to the N–H stretching frequency of amide group of nylon-6,6 [32]. An assembly of small peaks in the region 500–950 cm^{-1} is due to the superposition of metal–oxygen stretching vibrations. These characteristic stretching frequencies are also in close resemblance with the inorganic precipitate, i.e. Sn(IV) phosphate (Fig. 4a) and Nylon-6,6 Sn(IV) phosphate (Fig. 4b), indicating the binding of inorganic precipitate with organic polymer and formation of 'polymeric-inorganic' fibrous Nylon-6,6 Sn(IV) phosphate.

The X-ray powder diffraction pattern of this cation-exchanger (sample S-4, as-prepared) recorded on powdered sample exhibited no peak in the spectrum (Fig. 5) that suggesting an amorphous nature of the composite material.

SEM photographs of Sn(IV) phosphate and Nylon-6,6 Sn(IV) phosphate obtained at different magnifications (Fig. 6) indicating the binding of inorganic ion-exchange material with organic polymer. It has been revealed that after binding of organic polymer with Sn(IV) phosphate, the morphology has been changed.

As evident from the thermogravimetric analysis curve (Fig. 7) of Nylon-6,6 Sn(IV) phosphate fibrous cation-exchanger initial weight loss of mass ~11% up to 200 °C, may be due to the loss of external water molecule present [33]. Slow weight loss observed between 200 °C to 350 °C may be due to the condensation of phosphate group to pyrophosphate groups. Further weight loss between 350 °C to 450 °C may be due to complete decomposition of the organic part of the material. At 450 °C onwards, a smooth horizontal section which represents the complete formation of the oxide form of the material. A broad peak at ~500 °C in DTA curve shows the reaction is exothermic during the change of phase of the material.

In the composite cation exchange material Nylon-6,6 Sn(IV) phosphate the fixed anions (phosphate and amine group) are in electrical equilibrium with mobile cations in the interstices of the polymer. While the mobile anions are more or less excluded from the polymer matrix because of their electrical charge, which is identical to that of fixed ions. Due to exclusion of the co-ions, the material permits transfer of cations only.

In order to find out the selectivity of this composite material (S-10) for particular metal ions, distribution studies for 12 metal ions were performed in 13 solvent systems. The distribution studies (Table 4) showed that K_d values varied with the nature and composition of contacting solvents. It was observed from the sorption studies (K_d values) that the composite has a maximum selectivity towards Hg^{2+} because mercury was highly adsorbed in all solvents, while remaining metal ions were poorly adsorbed.

$$[Sn(HPO_4)_2\cdot(-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-)]^- + Hg^{2+}$$
$$\downarrow$$
$$[Sn(HPO_4)_2\cdot(-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-]^-\cdots Hg^{2+}.$$

On the basis of Distribution studies, the composite cation-exchanger was used as an electroactive component in the preparation of a heterogeneous ion-selective membrane electrode sensitive to Hg(II) ions. When membrane of such materials is placed between two electrolyte solutions of the same nature, at same pressure and temperature, but at different concentrations, a small number of ions (to which membrane is selective) pass from the solution of higher concentration through the membrane to that of lower concentration, thus producing an electrical potential difference i.e. membrane potential that can be used for electroanalytical studies.

A number of samples for the Nylon-6,6 Sn(IV) phosphate membranes were prepared with different amounts of Araldite and checked for the mechanical stability, surface uniformity, material distribution, cracks and thickness etc. But the membranes obtained with 50% Araldite (w/w) were found to be good, and show the best mechanical stability as well as electro-chemical performance.

The thickness, swelling, porosity, water content capacity etc. of the Nylon-6,6 Sn(IV) phosphate cation-exchanger membrane was investigated and the results are summarized in Table 6. It was observed that as the amount of electroactive component of the membrane i.e. Nylon-6,6 Sn(IV) phosphate increased, the thickness, swelling, water content, porosity increased. Thus, the low orders of water content, swelling and porosity with less thickness of this membrane suggest that the interstices are negligible and diffusion across the membrane would occur mainly through the exchange sites. Hence, membrane sample M-1 (thickness 0.16 mm) was selected for the preparation of an ion-selective electrode for further studies. However, further various characteristics are necessary for a membrane ion-selective electrode to be considered as a suitable sensor for the quantitative measurement of ions. The most important characteristics are the slope, working concen-

Table 6
Characterization of an ion-exchanger membrane.

Nylon-6,6 Sn(IV) phosphate composite material	Thickness/mm	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
M-1	0.16	1.06	0.210	No swelling
M-2	0.20	2.12	0.244	No swelling

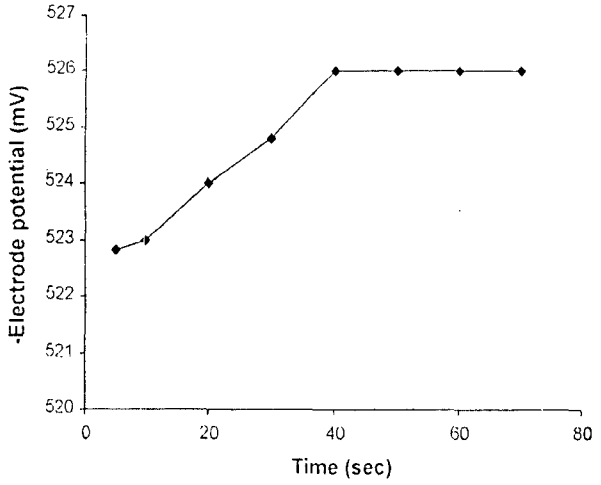

Fig. 9. Time response curve of Nylon-6,6 Sn(IV) phosphate membrane electrode.

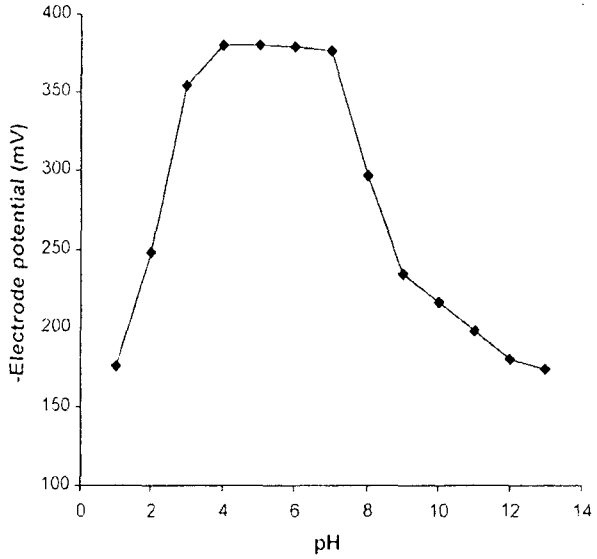

Fig. 10. Effect of the pH on the electrode response of Hg^{2+} ion-selective Nylon-6,6 Sn(IV)phosphate membrane electrode.

tration range, response time, pH, selectivity and life span of the membrane electrode.

The potentiometric response of the membrane electrode prepared from membrane sample M-1 over a wide concentration range 10^{-1}–10^{-9} is shown in Fig. 8. The electrode showed a linear Nernstian response for Hg(II) ions in the concentration range 1×10^{-1} to 1×10^{-7} M with an over Nernstian slope of 28.09 mV per decade change in concentration. The limit of detection of the electrode, as determined according to the IUPAC recommendation [34,35] form the intersection of two segments of calibration curve, was 1×10^{-7} M. An over-Nernstian response in electrode of this kind is common [36–38].

It was observed that the response time of the Nylon-6,6 Sn(IV) phosphate membrane electrode was 40 s as shown in Fig. 9. It is very important that the performance of any ion-selective electrode should be checked soon every time before using it for any analytical purpose.

For the present Nylon-6,6 Sn(IV) phosphate membrane electrode, it was observed that the measured potential of Hg^{2+} ions in a given concentration range of 10^{-1}–10^{-9} M was reproducible within ±1 mV, and there was no significant change in the slope of the Nernst plot during the experiment over a time period of 1 month. This suggests a longer electrode life and a stable electrode performance.

The performance of the proposed Hg(II) ion-selective membrane electrode based on the organic–inorganic composite cation-exchanger polyaniline Sn(IV) phosphate is comparable [39–48], and even better in many respects, such as the slope, response time, linear concentration range, lifetime, pH range and selectivity. It is clear from Fig. 10 that the pH influenced the response characteristics of the proposed Hg(II) ion-selective membrane electrode that the potential remained unchanged within the pH range 4–7. After that pH, the electrode behaved in an erratic manner, which may be because mercury ions formed a hydroxyl complex and precipitated. Thus, we can say that the optimum pH range of operation of this electrode was pH 4–7.

The selectivity of the electrode is determined in terms of potentiometric selectivity coefficient, $K^{POT}_{Hg,M}$, by mixed solution methods [37]. The selectivity coefficient values shown in Table 7 indicate the extent to which a foreign ion (M^{n+}) interferes with the response of the electrode towards its primary ion (Hg^{2+}). The selectivity coefficients of various cations for the Hg(II) ion-selective Nylon-6,6 Sn(IV) phosphate membrane electrode were determined which reveal that the membrane electrode is highly selective for Hg(II) ions over a number of cations as shown in Fig. 11.

The selectivity coefficients of bivalent and trivalent metal ions, like Co(II), Zn(II), Cd(II), Pb(II), Cu(II), and Fe(III), showed somewhat

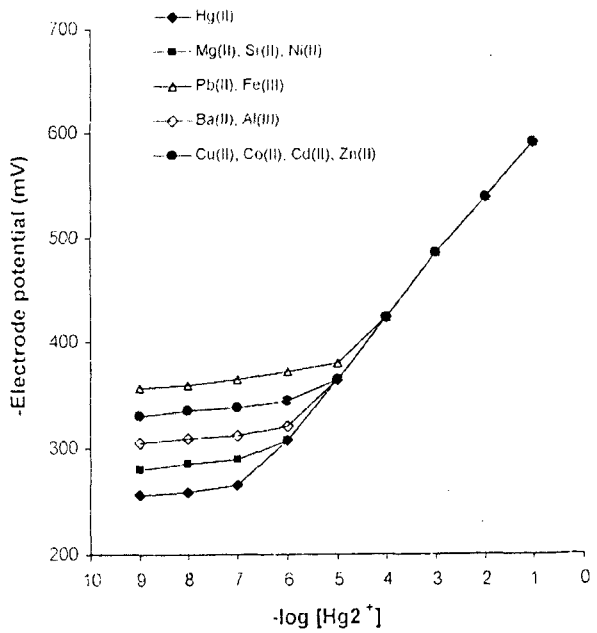

Fig. 11. Curves for Nylon-6,6 Sn(IV)phosphate membrane electrode in Hg(II) solution and in solution of interfering ions with Hg(II).

Table 7
Selectivity coefficients, $K^{POT}_{Hg,M}$, of various interfering ions (M^{n+}).

M^{n+}	$K^{POT}_{Hg,M}$
Pb^{2+}	1×10^{-2}
Cu^{2+}	5×10^{-2}
Fe^{3+}	1×10^{-2}
Zn^{2+}	5×10^{-2}
Co^{2+}	5×10^{-2}
Cd^{2+}	5×10^{-2}
Ba^{2+}	1×10^{-1}
Al^{3+}	1×10^{-1}
Mg^{2+}	1×10^{-1}
Ni^{2+}	1×10^{-1}
Sr^{2+}	1×10^{-1}

higher values and interfered to a very little extent. However, Ba(II), Mg(II), Sr(II), Ni(II) and Al(III) showed very low selectivity coefficients, and hence interference was found to be negligible. Therefore, despite their large selectivity coefficients, these ions would not disturb the functioning of the Hg(II)-selective membrane electrode. Thus, the results revealed that the electrode was selective for Hg(II) in the presence of interfering cations. Therefore, it is understandable the Nylon-6,6 Sn(IV) phosphate interacts relatively strongly with Hg(II) ions, and can be successfully used as a sensing agent for mercury-selective electrodes.

5.1. Analytical application

The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometeric titration of a 0.01 M $Hg(NO_3)_2$ solution against an EDTA solution as a titrant. The results are shown in Fig. 12. A 5 ml $Hg(NO_3)_2$ solution was pippeted out in a beaker, and its volume was raised up to 20 ml by adding demineralized water. This solution was titrated against an EDTA solution; the electrode potential was measured after each addition of 0.5 ml of EDTA. The addition of EDTA causes a decrease in potential as a result of the decrease in free Hg(II) ion concentration due to formation of a complex with EDTA. The amount of Hg(II) ions in solutions can be accurately determined from the resulting neat titration curve providing a sharp end point.

Nylon-6,6 Sn(IV) phosphate, Hg^{2+} ion-selective membrane electrodes were also applied to direct measurements of Hg^{2+} in the drain water collected from Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India. The samples were collected by a routine technique from five different locations of drains, and preserved with HNO_3, stored in glass bottles and analyzed within 12 h after collection. Since the samples contained particulate matters, they were centrifuged, and the potentials were measured after adjusting the pH to ~4 with HNO_3 or NH_3. Three replicate measurements were made to obtain the Hg(II) contents in five samples with this electrode using the membrane sensor's calibration graph. The concentration of mercury in the sample was $\sim 10^{-6}$ M, and the reproducibility of the results was checked up to three times.

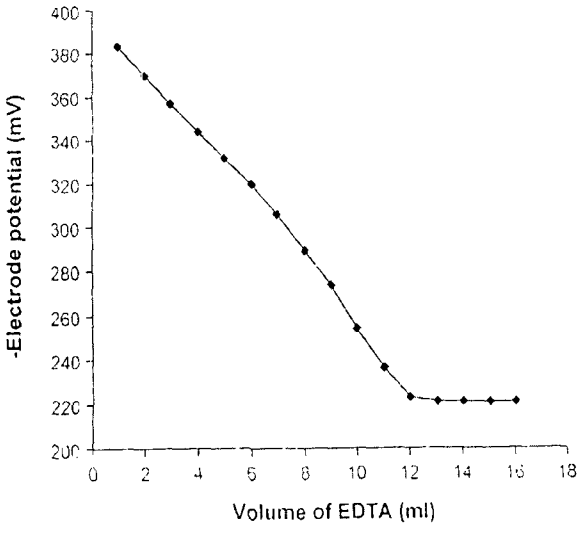

Fig. 12. Potentiometric titration of Hg(II) against EDTA solutions using Nylon-6,6 Sn(IV)phosphate membrane electrode.

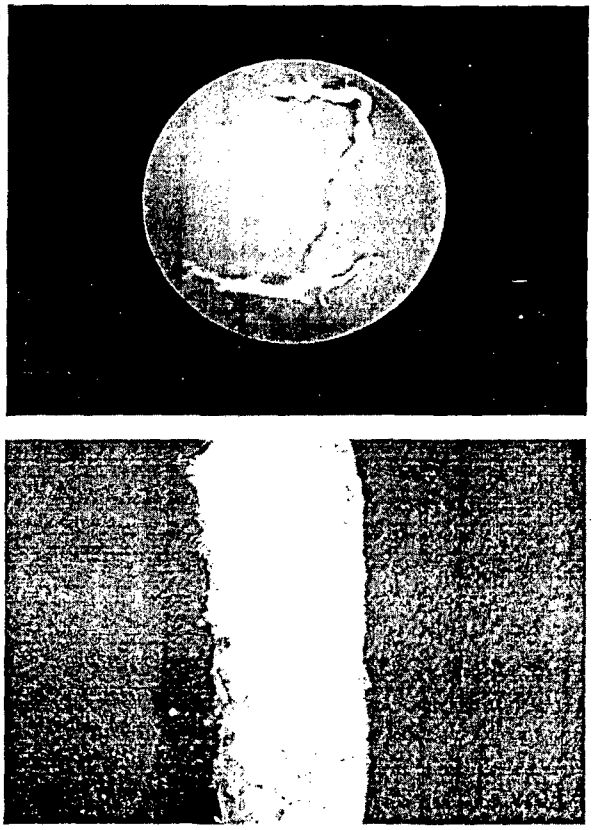

Fig. 13. (a) Photograph of a single fiber of Nylon-6,6 Sn(IV) phosphate composite cation-exchanger. (b) Photograph of the strip of Nylon-6,6 Sn(IV) phosphate composite cation exchanger.

Nylon-6,6 Sn(IV) phosphate is a white color fibrous type material. This material can be also used in making indicator strips for qualitative and approximately quantitative determination of heavy metals. PAN indicator strips of Nylon-6,6 Sn(IV) phosphate suggest the sensitivity of some heavy metals like Cu(II), Pb(II), Hg(II), Fe(II) in the concentration range of 2 ppm to 200 ppm (Table 5). The change in color may suggest an approximate amount of heavy metals in an unknown sample. Photographs of a single fiber of Nylon-6,6 Sn(IV) phosphate and a PAN indicator strips of the composite cation-exchanger are shown in Fig. 13.

Acknowledgements

The authors are thankful to Department of Applied Chemistry, Z.H. College of Engineering and Technology, A.M.U. (Aligarh) and Ministry of Environment and Forest (India) for providing research facilities. Assistance provided by the R.S.I.C. Bombay, I.I.T. Delhi and I.I.T. Roorkee to carry some instrumental analysis.

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Adsorption and Electroanalytical Studies of a Poly(*o*-toluidine)/Zirconium(IV) Phosphate Nanocomposite for Zinc(II) Dimethyldithiocarbamate

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Received 9 January 2010; accepted 26 March 2010
DOI 10.1002/app.32658
Published online 00 Month 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The adsorption behavior of zinc(II) dimethyldithiocarbamate (Ziram) was studied on the surface of a poly(*o*-toluidine)/zirconium(IV) phosphate nanocomposite cation exchanger. A spectrophotometric method based on the conversion of Ziram into a copper dimethyldithiocarbamate complex was applied for the study of Ziram at the maximum absorption wavelength of 437 nm. A Ziram-sensitive membrane electrode was fabricated with poly (*o*-toluidine)/zirconium(IV) phosphate (an electroactive composite material). The sensitivity of Ziram for the composite cation-exchange material was monitored with potentiometric methods. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2010

Key words: adsorption; composites; electrochemistry; ion exchangers; nanocomposites

INTRODUCTION

Pesticides of the carbamate family have been progressively replacing more persistent species (mainly organophosphates) because of their low persistence in the environment, biological activity, and large spectrum of utilization. They are used as insecticides, fungicides, nematocides, miticides, and molluscicides. Dithiocarbamates are widely used in agriculture as fungicides and in the rubber industry as vulcanization accelerators and antioxidants. Metal salts of dithiocarbamates are more effective as fungicides because the toxicity of the dithiocarbamates is increased by the metal. Dithiocarbamates have also been studied in vegetable foodstuffs with high-performance liquid chromatography,[1] extraction voltammetry,[2] and titrimetry.[3] Capillary electrophoresis was used by Rossi and Rotilio[4] for the qualitative and quantitative analysis of different carbamates, thiocarbamates, and dithiocarbamates. However, all these methods suffer from the following disadvantages: (1) methods other than gas chromatography are indirect and time-consuming and have low sensitivity, and (2) gas chromatography methods are sensitive but suffer from a lack of selectivity because all dithiocarbamate pesticides evolve carbon disulfide during acid hydrolysis.

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Journal of Applied Polymer Science, Vol. 000, 000–000 (2010)

Zinc(II) dimethyldithiocarbamate (Ziram) is an agricultural fungicide. It can be applied to the foliage of plants, but it is also used as a soil and/or seed treatment. Ziram is used primarily on almonds and stone fruits. It is also used as an accelerator in manufacturing rubber, packaging materials, adhesives, and textiles and as a bird and rodent repellent. Ziram can cause skin and mucous membrane irritation. Humans with prolonged inhalation exposure to Ziram have developed nerve and visual disturbances.[5] Ziram is corrosive to eyes and may cause irreversible eye damage.[6]

Ziram has also been converted into molybdenum[7] and copper complexes.[8,9] The extraction of the molybdenum complex is slow, and complexation occurs in an acid medium. A simple, rapid, and sensitive spectrophotometric method based on the conversion of Ziram into a copper dimethyldithiocarbamate complex was applied in this work to study Ziram. However, the main objective of this research was to developed an electroanalytical method for making a Ziram-sensitive membrane electrode to find trace amounts of Ziram in water.

EXPERIMENTAL

Equipment and reagents

A digital pH meter (Elico, India), a potentiometer, and an SL 164 double-beam ultraviolet–visible spectrophotometer (Elico) were used. Solutions (0.1*M*) of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and phosphoric acid (H_3PO_4) of different molarities were

prepared in 4*M* HCl and demineralized water (DMW), respectively. Solutions of 20% (v/v) *o*-toluidine (C_7H_9N) and 0.4*M* ammonium persulfate [$(NH_4)_2S_2O_8$] were prepared in 2*M* HCl.

Preparation of the Ziram solutions

A stock solution of Ziram (1 g/L) was prepared by the dissolution of 100 mg of Ziram in NaOH (0.1*N*) and by dilution to 100 mL in a volumetric flask; further dilutions were performed with 0.1*N* NaOH as desired. Copper sulfate (1.0 g/L) was prepared by the dissolution of 0.1 g in 100 mL of distilled water, which was then acidified with 0.1 mL of concentrated sulfuric acid. An acetate buffer was prepared in distilled water by the dissolution of sodium acetate trihydrate (68 g; analytical-reagent grade; Merck) in water (400 mL) and by the adjustment of the pH to 4.5 through the addition of glacial acetic acid (25–30 mL; analytical-reagent grade; Merck); the total volume was 500 mL.

In a blank solution, a copper sulfate solution (1.0 mL) was added with an aqueous acetate buffer solution (1.0 mL) and Triton X-100 (2 mL), and the volume was increased to 10 mL with distilled water without the Ziram solution.

Preparation of the poly(*o*-toluidine)/zirconium(IV) phosphate composite cation-exchange material (adsorbent)

The nanocomposite cation exchanger was prepared by the sol–gel mixing of poly(*o*-toluidine), an organic polymer, into the inorganic precipitate of zirconium(IV) phosphate. In this process, when the poly (*o*-toluidine) gels were added to the white inorganic precipitate of zirconium(IV) phosphate with constant stirring, the resultant mixture was turned slowly into a greenish-black slurry. The resultant greenish-black slurry was kept for 24 h at room temperature.

Then, the poly(*o*-toluidine)-based composite gels were filtered off and washed thoroughly with DMW for the removal of excess acid and any adhering trace of $(NH_4)_2S_2O_8$. The washed gel was dried over P_2O_5 at 40°C in an oven. The dried product was washed again with acetone to remove oligomers present in the material and was dried at 40°C in an oven. The dried product was cracked into small granules and converted into the H^+ form via treatment with 1*M* HNO_3 for 24 h with occasional shaking; the supernatant liquid was intermittently replaced with fresh acid two to three times. The excess acid was removed after several washings with DMW and finally dried at 50°C. A particle size of approximately 125 μm for the composite cation exchanger was obtained via sieving, and the material was stored in desiccators.[10]

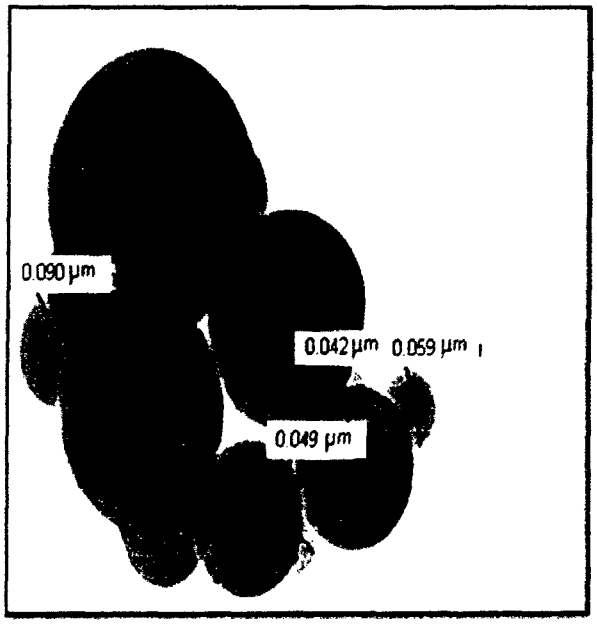


Figure 1 TEM image showing the particle size of the poly(*o*-toluidine)/zirconium(IV) phosphate cation-exchange material.

Transmission electron microscopy (TEM) studies

TEM studies were carried out to determine the particle size of the poly(*o*-toluidine)/zirconium(IV) phosphate composite cation-exchange material, as shown in Figure 1. From the TEM studies, it is clear that the poly(*o*-toluidine)/zirconium(IV) phosphate cation-exchange material had a particle size range of 42.0–100.0 nm; that is, the material particle size was in the nanorange.

Adsorption of Ziram onto the poly(*o*-toluidine)/zirconium(IV) phosphate cation exchanger

To different 100-mL conical flasks, 25-mL Ziram solutions of different concentrations (0.5–10 ppm) were added; 0.5 g of the adsorbent [poly(*o*-toluidine)/zirconium(IV) phosphate] was also added. The flasks were closed and allowed to stand for 1 h with intermittent shaking. Then, the contents were filtered, and 1 mL of the filtrate of each concentration was placed into another conical flask. To each flask, a copper sulfate solution (1.0 mL), an aqueous acetate buffer solution (1.0 mL, pH = 4.5), and Triton X-100 (2 mL) were added, and the volume was increased to 10 mL with distilled water. The mixture was shaken vigorously for 2–3 min. The absorbance of the solution was measured at 437 nm against a reagent blank.[11]

The adsorption percentage from a standard solution was calculated as follows:

$$\text{Adsorption}(\%) = C_0 - C_e/C_0 \times 100 \qquad (1)$$

TABLE I
Adsorption Percentage of Ziram Before and After Adsorption onto the Poly(*o*-toluidine)/Zirconium(IV) Phosphate Cation Exchanger

Sample	Concentration (ppm)	Initial absorbance before adsorption	Absorbance after adsorption	Adsorbent (g)	Adsorption (%)
1	0.5	0.012	Completely adsorbed	0.5	100
2	0.6	0.016	Completely adsorbed	0.5	100
3	0.8	0.018	Completely adsorbed	0.5	100
4	1.0	0.0229	0.001	0.5	95.6
5	2.0	0.0592	0.019	0.5	84.7
6	3.0	0.0732	0.015	0.5	79.5
7	4.0	0.0976	0.022	0.5	77.5
8	6.0	0.1472	0.036	0.5	75.5
9	8.0	0.1995	0.055	0.5	72.4
10	10	0.253	0.095	0.5	62.5

where C_0 and C_e are the absorbances before and after adsorption on the cation exchanger, respectively. The adsorption percentages of Ziram before and after adsorption onto the poly(*o*-toluidine)/zirconium(IV) T1 phosphate cation exchanger are listed in Table I.

Absorption spectra

F2 Figure 2 shows the absorption spectrum of Ziram as a copper(II) dimethyldithiocarbamate complex dissolved in Triton X-100 against a reagent blank and the spectrum after adsorption onto the cation exchanger.

Preparation of the Ziram pesticide-sensitive membrane electrode

The ion-exchange membrane was prepared according to the procedure of Coetzee and Benson.[12] The poly(*o*-toluidine)/zirconium(IV) phosphate cation exchanger (100 mg), an electroactive material, was ground into a fine powder and was mixed thoroughly with Araldite (Ciba–Geigy India, Ltd.; 100 AQ6 mg) in a 1 : 1 (w/w) ratio to make a homogeneous paste, which was then spread between the folds of Whatman no. 42 filter paper. The phase of the AQ6 exchanger and Araldite was kept under a pressure of 2 kg cm^2 for 24 h and allowed to dry. One sheet of the master membrane with a thickness of 0.16 mm was prepared. This sheet was dipped into distilled water to remove the filter paper. After it dried, the membrane sheet was cut into the shape of a disc with a sharp-edge blade.

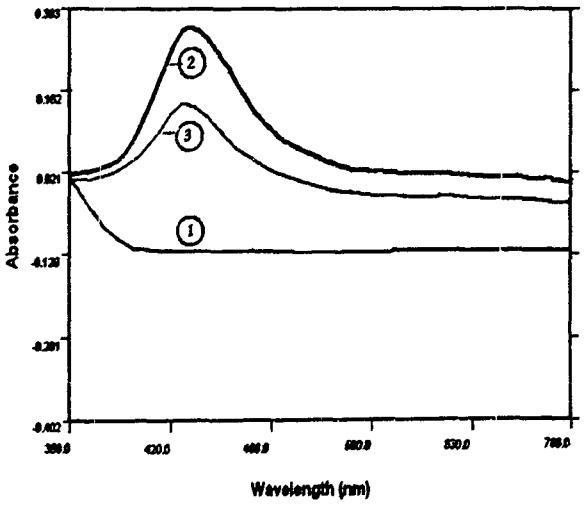


Figure 2 Absorption spectra of (1) a blank solution, (2) the Ziram/copper (II) dimethyldithiocarbamate complex in Triton X-100 against a reagent blank before adsorption, and (3) the Ziram/copper (II) dimethyldithiocarbamate complex after adsorption onto the poly(*o*-toluidine)/zirco- AQ4 nium(IV) phosphate cation exchanger.

Fabrication of the pesticide-sensitive membrane electrode of the poly(*o*-toluidine)/zirconium(IV) phosphate cation exchanger

The membrane electrode was fabricated as reported in a previous study.[13]

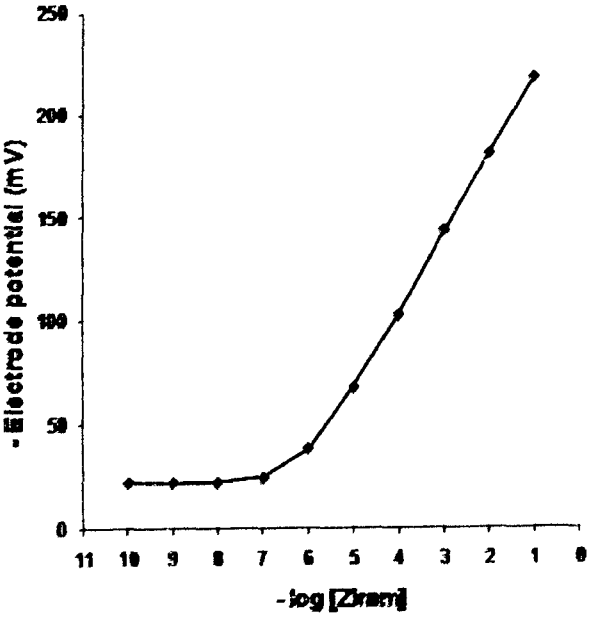


Figure 3 Calibration curve for the Ziram-sensitive membrane electrode. [Color figure can be viewed in the online AQ5 issue, which is available at www.interscience.wiley.com.]

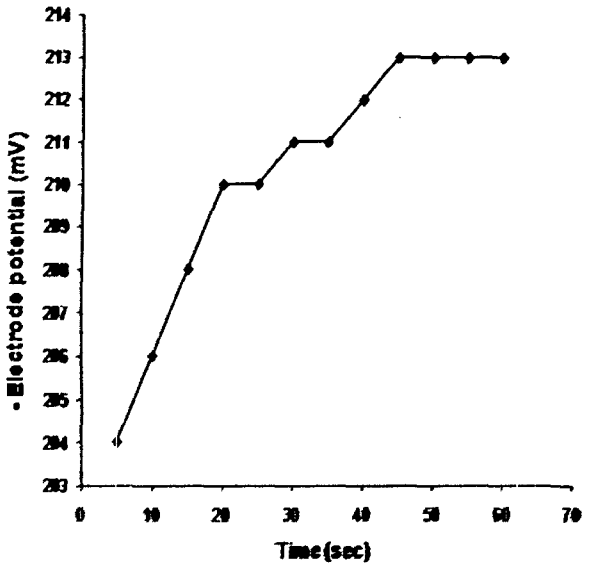


Figure 4 Time–response curve for the Ziram-sensitive membrane electrode.

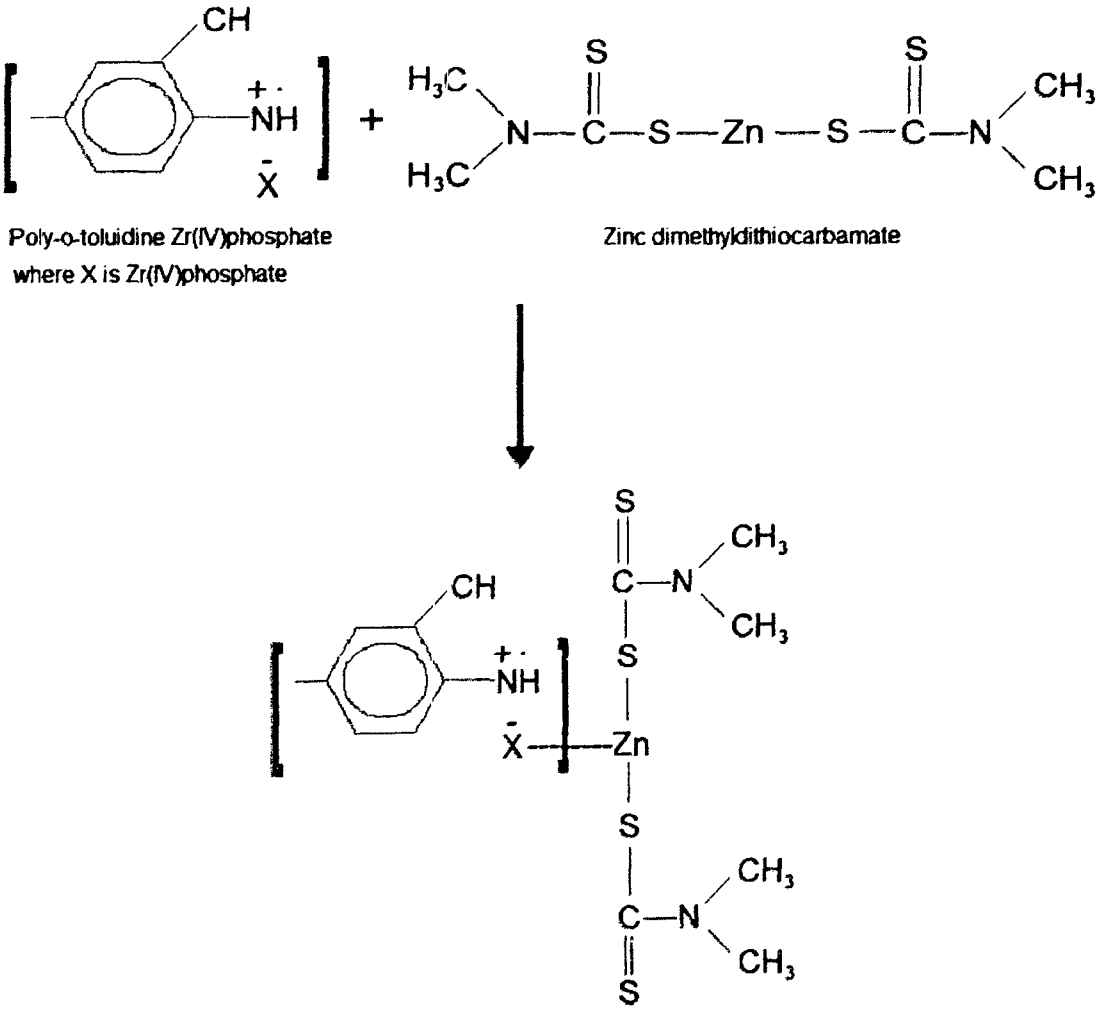
The following parameters were evaluated to study the sensitivity of the electrode to Ziram: the lower detection limit, electrode-response curve, and response time.

Electrode response or membrane potential

A series of Ziram solutions of various concentrations ranging from 10^{-1} to $10^{-10}M$ were prepared. The external electrode and the pesticide-selective membrane electrode were plugged into a digital potentiometer, and the potentials were recorded. First, the electrode was soaked in a $1 \times 10^{-1}M$ solution of Ziram for 2–3 days and for 1 h before use. When the electrode was not in use, it was kept in a $1 \times 10^{-1}M$ solution. The measured potential is plotted against selected concentrations of the pesticide in solution in Figure 3. F3

Response time

The electrode was first dipped into a $1 \times 10^{-2}M$ solution of Ziram and then into a $1 \times 10^{-1}M$ solution. The potential of the solution was read at 0 s; just



ED1 **Scheme 1**

after the electrode was dipped into the second solution, the potential was recorded subsequently at the interval of 5 s. The potentials versus the time are F4 plotted in Figure 4.

RESULTS AND DISCUSSION

Poly(*o*-toluidine)/zirconium(IV) phosphate is an established nanocomposite cation exchanger.[10] Its excellent ion-exchange behavior is due to the presence of strong phosphate groups (co-ions) present in the matrix of the composite, which have electrostatic attraction for positive cations (counterions). Ziram, a zinc-based dimethyldithiocarbamate, was adsorbed completely up to a concentration of 0.8 ppm and retained 60% of its adsorption up to 10 ppm (Table I). The mechanism of S1 adsorption is presented in Scheme 1.

Poly(*o*-toluidine)/zirconium(IV) phosphate is formed by ionic interactions between the radical cations of poly(*o*-toluidine) and anionic groups of zirconium(IV) phosphate.[10] Phosphate groups of zirconium(IV) phosphate behave as co-ions for the cation-exchange material and have an electrostatic potential for metal present in the carbamate fungicide. However, the nanoparticle size of the material (24.0–100 nm) increases the surface area of the adsorbent, and this results in the maximum adsorption of the pesticide.

On the basis of the adsorption behavior of Ziram on the surface of poly(*o*-toluidine)/zirconium(IV) phosphate, a Ziram-sensitive, heterogeneous-precipitate membrane electrode was prepared from the poly(*o*-toluidine)/zirconium(IV) phosphate cation-exchange material, and it yielded a linear response in the range of 1×10^{-1} to $1 \times 10^{-7}M$. The working concentration range was 1×10^{-1} to $1 \times 10^{-10}M$ (Fig. 3) for Ziram with a lower Nernstian slope of 28.1 mV per decade change in the Ziram concentration. The limit of detection, determined from the intersection of the extrapolated segments of the calibration graph,[14] was found to be $1 \times 10^{-7}M$.

The promptness of the response of the pesticide-sensitive electrode was also determined. The average response time was defined as the time required for the electrode to reach a stable potential. The response time of the membrane sensor was approximately 45 s (Fig. 4). The membrane could be successfully used up to 1 month without any notable change in the potential; during this time, the potential slope was reproducible within ±1 mV per concentration decade. When a drift in the potential was observed, the membrane was re-equilibrated with a $1 \times 10^{-1}M$ solution for 1 week.

CONCLUSIONS

In this research, a nanocomposite cation exchanger, poly(*o*-toluidine)/zirconium(IV) phosphate, showed excellent adsorption of Ziram in the range of 0.8–10 ppm. A TEM photograph showed that the particle size of the composite material was between 42.0 and 100.0 nm, so the material could be considered a nanocomposite. The sensitivity of Ziram toward the membrane electrode of the poly(*o*-toluidine)/zirconium(IV) phosphate nanocomposite cation exchanger was indicated by a change in the potential with a change in the concentration. The membrane electrode possessed a quick response time of only 45 s with a slope of 28.1 mV per decade change in the concentration range of 1×10^{-1} to $1 \times 10^{-7}M$. The membrane electrode showed a detection limit of good reproducibility and could be used successfully up to 1 month.

The authors are thankful to the Department of Applied Chemistry of Aligarh Muslim University (Aligarh, India) for providing research facilities. Special thanks are given to H. S. Rathore for his guidance during various stages of the research. The authors are also thankful to the Indian Ministry of Environment and Forests for providing facilities to carry out the research.

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